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The Corpuscular Theory of the Primary Cosmic Radiation

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(Received July 29, 1935)

The approximately exponential law of cosmic-ray absorption is, at first sight most readily accounted for by the hypothesis that the primaries are composed of photons. However, latitude and asymmetry effects demand that at least 31 percent of the primary radiation be attributed to charged particles. This is enough to spoil the exponential law given so readily by photons unless the charged particle hypothess be developed so as to give an exponential law. The naïve hypothesis that the exponential law is to be provided by a suitable range of penetrations of the incoming rays, resulting from a corresponding range of energy distribution is found untenable, mainly because such a hypothesis would lead to a condition in which the quality of the measured radiation was independent of altitude. The paper reviews a hypothesis already published by the writer to the effect that the primary rays produced secondaries in number per centimeter of path proportional to the primary energy. These secondaries perpetuate the primary path. They represent the rays actually measured, and the theory gives an exact exponential law. The theory gives, in fact, a constant "apparent" coefficient of absorption of the measured effect which is independent of the primary energy. This result requires modification to harmonize with the data on the latitude and directional effects. It is shown that harmonization is provided by a modification of the theory which permits an increase of coefficient of apparent absorption with decrease of primary energy. It is found that such a modification can be readily made in more ways than one. It is then shown that the apparently contradictory phenomenon involved in the "hardening" of the average radiation with passage through matter can readily be accounted for by adding to this hypothesis already made, the known fact of a distribution of energies in the incoming primary corpuscular radiation. A modification of the foregoing theory permits the "apparent" primaries referred to in it to be really photons produced by impact of true primary charged particles with the upper atmosphere. The writer reviews a former hypothesis made by him with regard to the dependence of shower production and atomic burst production in lead, a hypothesis designed to provide an explanation that these phenomena increase with altitude much more rapidly than does the measured cosmic-ray intensity. It results that the extension of the main theory concerned with absorption of the primary energy when combined with the hypothesis concerning burst and shower production results in harmonization of all the details of these phenomena as far as they are known. A list of eleven facts concerned with cosmic-ray absorption, latitude and directional effects, burst and shower production is made. The list comprises all of the outstanding facts concerned with the subject; and it is shown that the extended theory harmonizes all of them.

INTRODUCTION

THE purpose of this paper is to amplify the views stated by the writer in former communications as to the nature of the primary cosmic radiation, and to develop them to the point of correlating in one consistent story the experimental phenomena upon which they have bearing.

Probably the most powerful argument in favor of photons as primary rays arises from the relative ease with which such an assumption accounts for the approximately exponential law of absorption shown by the cosmic-ray intensity. However, the latitude and directional effects seem to demand that, even as a minimum, such

a large[1] percentage of the primary radiation shall be of the charged corpuscular type that the simple explanation of the exponential law inherent in the assumption of photons becomes spoiled; and it becomes necessary to seek in the corpuscular hypothesis itself an explanation of a similar type of absorption law. With the situation at this stage, it becomes of interest to see how far the various facts concerning cosmic-ray phenomena may be correlated completely by the assumption that the entire primary cosmic radiation is of the charged corpuscular type.

The Conventional View as to the Properties of a Primary Corpuscular Radiation, and the Difficulties Associated with that View

The primitive picture of the behavior of a primary charged corpuscular radiation represents each of its entities, or rays, as producing ionization continually along its path at the rate of about 30 ions or more per centimeter of path (at sea level, atmospheric pressure), and losing, at each act, an amount of energy very small compared with the total energy possessed by the ray. Such a condition is the determining feature which gives to the ray a definite range, characteristic of its energy, and sensibly constant for all rays of the same type and energy. The increase of ionizing efficiency at the end of the range is a phenomenon associated with only the last meter or so of the range at normal pressure, and may be left out of consideration in the matters which concern us here. On this primitive view of the nature and properties of the primary corpuscular radiation, penetration of different numbers of the rays through different thicknesses of the atmosphere, for any assigned direction, is to be secured only by the existence of a range of energy in the particles which enter the atmosphere from above; and the existence of an exponential law for the measured intensity in any direction necessitates a corresponding distribution of numbers of rays among the energies calculated to give such a law. Apart from the artificiality[2] of postulating such an arbitrary situation, and in contrast to what a superficial picture of the phenomena would suggest, the result, if secured, would be accompanied, as the writer has shown[3] by a condition in which the *quality* of the radiation, as symbolized by the energy distribution among the rays would be the same at all altitudes. Such a condition would result in an exact proportionality between the intensity of the radiation at different altitudes (as measured by number of rays per second per square centimeter per unit solid angle), suitably averaged for all angles, and the frequency of occurrence of any phenomenon initiated by the primary radiation. Thus, for example, on this hypothesis, we should expect that the number of particle showers, or atomic bursts, of any size, produced by the cosmic radiation under specified conditions in lead would increase with altitude in exact proportion to the directionally averaged intensity of the radiation, whereas, as a matter of fact, the experiments of C. G. and D. D. Montgomery[4] of this laboratory, on showers of large size, show that shower production in lead increases with altitude more nearly in proportion to the square of the average cosmic-ray intensity as measured by ionization in a closed chamber. Similar conclusions result from the work of R. D. Bennett, G. S. Brown and H. A. Rahmel.[5] These experiments practically *demand* a theory which causes the quality of the radiation to vary with altitude; and they are supported by similar experimental results obtained, for small showers, by T. H. Johnson[6] and by B. Rossi and S. de Benedetti.[7]

[1] The latitude observations at high altitudes seem to demand that at least 25 percent of the cosmic-ray intensity, measured at high latitudes, shall be initiated by primaries of the charged corpuscular type. This lower limit becomes increased to 31 percent by the azimuthal, equatorial asymmetry measurements of T. H. Johnson, which are able to lay hold of a contribution from the equatorial intensity and designate it also as corpuscular. Even this 31 percent is still but a lower limit.

[2] A certain amount of the artificiality is removed on realizing that the necessary law of distribution relating numbers of rays to energy is an exponential one; and an exponential law is not an unreasonable one.

[3] W. F. G. Swann, Phys. Rev. **47**, 575 (1935).

[4] C. G. and D. D. Montgomery, Phys. Rev. **47**, 429 (1935).

[5] R. D. Bennett, G. S. Brown and H. A. Rahmel, Phys. Rev. **47**, 437 (1935).

[6] T. H. Johnson, Phys. Rev. **45**, 569 (1934).

[7] B. Rossi and S. de Benedetti, Ricerca Scient. **5**, 1 (1934).

Modification of Corpuscular Theory—Elementary Form

It has been shown by the writer,[8] that a variation of quality with altitude may be secured by a condition in which the primary rays come right through the atmosphere, losing energy on the way, and producing long range secondaries all along their paths.[9] If it is supposed that these secondaries perpetuate the direction of motion of the primaries,[10] and that they are the entities actually measured in our Geiger counters, *an exponential law for the measured intensity in any assigned direction* is secured[8] provided that we assume that the number of such secondaries produced per centimeter of path of the primary is proportional to the energy of the primary. It results, further, that if production of showers or atomic bursts in lead, or other elements of high atomic weight, depends upon a higher power of the ray energy than the first,[11] shower and burst production will increase with altitude more rapidly than does the measured radiation, so that such experiments as those of the Montgomerys, receive a rational interpretation. In line, moreover, with this idea, it is to be expected that the primary rays, which, at the earth's surface, travel in a direction of say 45° to the zenith, will be less efficient in the production of atomic bursts than will vertical rays, on account of the smaller average energy of the former resulting from the greater distance they have traveled through the atmosphere. An experiment confirming this view has[12] recently been performed by D. Cowie and the writer. This experiment explains, moreover, the oft-quoted observation to the effect that shower particles travel, for the most part, in a vertical direction, or in directions symmetrical to the vertical, a conclusion difficult to understand if an appreciable number of the primaries with direction inclined to the vertical are effective in producing atomic bursts.

Bearing of the elementary theory upon the observed energies of cosmic-ray particles in relation to the energies suggested by the observed influence of the earth's magnetic field

The simple theory, involving proportionality between energy and energy loss per centimeter of path (at normal pressure), gives the *same measured coefficient of absorption regardless of the energy of the primaries*, as is implied, indeed, in the fact that it gives the exponential law. Moreover, the theory makes that *coefficient of absorption the same as the coefficient of absorption of the primary energy*.[8] The latter fact is of interest because it suggests, between the energies of the rays entering the atmosphere and the energies as measured at sea level, a relation calculable in terms of the relation between the cosmic-ray intensity at, or near, the top of the atmosphere and the corresponding intensity at sea level. The energies of the primary rays should, in fact, increase with altitude in the same proportion as the intensity as measured by counters increases. The recent stratosphere flight made by Major W. E. Kepner, Captain A. W. Stevens, and Captain O. A. Anderson, and also that made by Professor and Mrs. Jean Piccard, both with Geiger-counter apparatus designed by G. L. Locher and the writer, agree in showing that the vertical intensity, when extrapolated to the top of the atmosphere, is about 90 times the sea-level value.[13] The minimum electron energies

[8] W. F. G. Swann, Phys. Rev. **46**, 828 (1934).

[9] We wish to leave as wide a latitude as possible in the nature of the primary charged corpuscles. Moreover, there is no need for us to commit ourselves as to whether the production of the secondaries takes place in one act, or through intermediaries, such as short range photons.

[10] A very exact perpetuation of direction results from the principles of conservation of energy and momentum, provided that the energies of all the particles concerned are such that the mass of each is large compared with its rest mass, and provided that potential energy changes are negligible. (See W. F. G. Swann, J. Frank. Inst. **220**, 373 (1935).)

[11] In general, we might suppose that shower production is a function of the primary energy E, of the form $A_1E+A_2E^2+\cdots$, etc., where the A's are functions of the atomic number of the shower producing material. If A_2 were proportional to the atomic number, we might have a condition where the second term was negligible compared with the first for air, while, for lead, the first was negligible compared with the second.

[12] W. F. G. Swann and D. Cowie, Phys. Rev. **47**, 811 (1935). A full account of this investigation is given in Phys. Rev. **48**, 649 (1935).

[13] It is preferable to use the actual measured relative intensities as obtained by counters rather than the values obtained from published coefficients of absorption, or even those given by ionization measurements directly, since there is evidence, particularly from the stratosphere flights, that the ionization measured intensity does not increase in exact proportion to the intensity as measured by the number of rays, even when the latter are averaged appropriately for all angles. The lack of proportionality in question is, of course, only to be expected in view of the change of quality of the primary radiation with altitude.

necessary to permit vertical entry in opposition to the earth's magnetic field in these latitudes, is about 4.5×10^9 volts. The corresponding sea-level value would consequently be about 5×10^7 volts. This is a reasonable value in the light of the requirements demanded of it. The energy necessary for vertical entry of the equator is about 3×10^{10} volts, and if we could assume the same law of increase of intensity with altitude at the equator as at these higher latitudes, the corresponding minimum sea-level energy for the primaries would be about 3×10^8 volts. Of course, these are only *minimum* values for the energies of the vertical rays, and higher energies at entrance will correspond to higher sea-level energies. Apart from any other considerations, however, the principle here exemplified is sufficient to explain why cloud chamber experiments, made, of course, at low altitudes, have failed to reveal corpuscular energies as great as those which would be suggested by consideration of the requirements of the earth's magnetic field. Moreover, consideration of these matters serves to emphasize the importance of cloud chamber energy measurements at high altitudes.

An element of difficulty exists from a consideration of the case of rays which are inclined appreciably to the vertical, and which at entry are of sufficiently low energy to show azimuthal asymmetry. These rays, traveling as they do through distances in the atmosphere considerably greater than the vertical rays, would be expected to become reduced in energy at sea level to values below those permissible for the performance of their functions. However, this difficulty is only transitory, and will tend to disappear in the more complete formulation of the theory to be outlined below, according to which the effective coefficient of absorption of the energy, while of the same order of magnitude as that of the measured intensity, may be in actuality, somewhat less. Only a small difference between the two coefficients is sufficient to impart complete harmony into the situation; and, in the meantime, the orders of magnitude above-cited are significant in illustrating the basic fundamentals involved.

Formulation of a More Complete Theory

The elementary theory, formulated in the foregoing, while containing the fundamentals underlying the more complete theory, is naturally to be regarded only as an approximation to that theory. Before considering the more complete formulation, it will be well to make a list of the outstanding facts which it must be the purpose of any successful theory to correlate. The list is as follows:

(a) The intensity for any zenith angle θ obeys, approximately, an exponential law. According to the analysis of Millikan, 90 percent of the radiation, as measured by its ionizing effect, is to be accounted for by a component with coefficient of absorption μ equal to 0.5 per meter of water.

(b) Insofar as there is departure from the exponential law, it is in the direction of increased hardening (diminution of average coefficient of absorption) with distance traveled by the primary rays.

(c) The latitude diminution of cosmic-ray intensity in equatorial regions increases with altitude as shown by the experiments of A. H. Compton and his associates.

(d) The east-west effect defined as the ratio of the intensity, I_a, of the asymmetrical part of the radiation to the sum, I_0, of the intensities from east and west increases with altitude for a constant latitude, as shown by T. H. Johnson. It is of course understood that I_a and I_0 refer to a definite zenith angle.

(e) While the east-west asymmetry increases with zenith angle for small zenith angles, it finally attains a maximum and then diminishes with further increase of zenith angle as shown by the experiments of T. H. Johnson, Alvarez and Compton, and others.

(f) The east-west effect *increases* with decrease of latitude at a given altitude, as shown by T. H. Johnson.

Then we have a number of phenomena concerned with shower production or atomic bursts. They are:

(g) Calling $S(L)$ the number of showers or bursts of any character produced per unit volume in lead or other element of high atomic weight, and I the average intensity of the cosmic radiation, the experiments of the Montgomerys, and of Johnson and of Rossi, show that $S(L)/I$ increases with altitude.

(h) Calling $S(L)_\theta$ the number of showers produced per unit volume of lead by the cosmic rays received at the zenith angle θ, and I_θ the measured intensity of the rays at this angle, $S(L)_\theta/I_\theta$ diminishes with increase of θ. This results from the experiment performed by Mr. Cowie and myself, cited earlier.

(i) Writing R for the ratio of $S(L)/I$ at latitude $\varphi=\varphi_1$ to the corresponding value at $\varphi=0$ it appears that R is less than unity for all values of φ_1 at which observations have been made.

(j) If R_h is the value of R at h, and R_0 is the value at sea level, R_h/R_0 is greater than unity.

(k) The showers produced by rays from east and west show less asymmetry than do the east and west intensities themselves.

The phenomena under i, j, k result from measurements made by T. H. Johnson.

The existence of a law approximately exponential as required by (a) has been provided for by the elementary theory already cited. In fact, the theory provides for this law as an exact consequence. The fact (b) is not provided for in the elementary theory.

The elementary theory while accounting for an alteration of quality with altitude, provides for a coefficient of absorption which is the same for all energies and altitudes. Now it is fundamental to the theory of the action of the earth's magnetic field upon charged corpuscles that the effect of the field shall be greater the smaller the energy. Hence, phenomenon (c) tells us that the apparent coefficient of absorption for the more deviable, soft, low energy rays must be greater than for the less deviable, high energy, hard rays.[14] Hence, our theory must provide for an increase of coefficient of absorption with decrease of energy. If such is provided for, an explanation is provided immediately for (d), since the asymmetrical rays have, by the fundamentals of the theory of asymmetry, less energy than the others. By the same provision, (e) is also explained, since increase of zenith angle is equivalent to increase of primary path.[15] The phenomenon (f) is an immediate consequence of the known theoretical conclusion that the range of energies involved in the asymmetrical rays increases with decrease of latitude. While, therefore, it is in harmony with the theory proposed, it does not invoke any assistance from that theory, but stands on its own merits.

Thus, with a reservation as regards (b), which reservation will presently be removed, all of the phenomena (a) to (f) inclusive are consistent with an extension of the elementary theory in the direction of providing for an apparent coefficient of absorption which increases with decrease of energy of the primary rays.

Turning, moreover, to the phenomena of shower production and the like, phenomena (g) and (h) receive a natural explanation on the lines formulated by the writer,[8] to the effect that shower production in lead depends upon a power of the primary energy higher than the first,[11] or at any rate higher than that which determines the shower production in air, which in turn determines the apparent intensity as measured.

If, for purposes of mathematical illustration, we suppose that I is proportional to E^n, where E is the primary energy, and n is positive; and if, following the ideas already formulated with regard to shower or burst production in lead, we assume $S(L)$ proportional to E^{n+k}, we have that $S(L)/I$ is proportional to E^{n+k}/E^n, i.e., to E^k; and the quantity defined as R, under (i) is proportional to $(E_1/E_0)^k$, where, as under (i) subscript zero refers to the equator and subscript unity to the latitude $\varphi=\varphi_1$. Thus, since on the average E_1/E_0 is less than unity, R is less than unity, which is in harmony with the fact (i).

Again, if subscripts s and h refer, respectively, to sea level and to the altitude h, we have

$$R_h/R_s=\left[\frac{(E_1/E_0)_h}{(E_1/E_0)_s}\right]^k=\left[\frac{(E_1)_h}{(E_1)_s}\cdot\frac{(E_0)_s}{(E_0)_h}\right]^k.$$

Now if we introduce for the E's coefficients of absorption μ_1 and μ_0 we have

$$R_h/R_s=e^{kh(\mu_1-\mu_0)}.$$

If further, as already necessitated by the facts (c), (d) and (e) we permit an extension of the elementary theory in the direction of making the coefficient of absorption of primary energy increase with decreasing energy, then μ_1 is

[14] In the case of rays which do not obey a true exponential law, it is convenient to introduce the concept of an apparent coefficient of absorption applicable to any point, and defined, for that point, by $-\mu_a=(1/A)dA/dx=d/dx(\log A)$, where A is the quantity measured and dx is an element of path.

[15] An interesting correlation, largely independent of the detailed form of the theory, here suggests itself. If asymmetry could be plotted against zenith angle in the absence of absorption, a continually rising curve would be obtained. This curve may be called the true asymmetry curve. In practice, this curve is disturbed by atmospheric absorption, so that, with increasing zenith angle, it shows first an increase and then a decrease in asymmetry. Now, for two different altitudes at depths h_1 and h_2 below the top of the homogeneous atmosphere, the path length is the same for corresponding zenith angles θ_1 and θ_2 related by $h_1/\cos\theta_1=h_2/\cos\theta_2$. If, therefore, in plotting asymmetry against zenith angle, we should choose for each zenith angle θ an appropriate altitude h for the measurement given by $h=\text{constant}\times\cos\theta$, and if we should plot the asymmetries so obtained against the corresponding values of θ, the result would be a graph of asymmetry *versus* zenith angle, freed from effects of atmospheric absorption at least to the extent that all rays measured would have traversed the same thickness of air.

greater than μ_2 and R_h/R_s is greater than unity, which is in harmony with (j). In all of the foregoing, it should be recognized that the magnitude of k depends, in all probability, upon the size of the shower or burst.

Turning now to fact (k), if E_a refers to the average energy of the rays which determine asymmetry and if E refers to the average energy of all the rays coming in the directions concerned, the normal asymmetry is determined by, say, $(E_a/E)^n$ where, as before, n is a positive number which, as a matter of fact is nearly equal to unity. In line with our fundamental hypothesis as to the dependence of burst and shower production upon primary energy, we conclude that the asymmetry in the shower production in lead is determined by $(E_a/E)^{n+k}$. Hence, regardless of the value of n since E_a is less than E we have, for the showers or burst, an asymmetry which is *less than the normal asymmetry for the intensity*, the ratio of the two being in fact $(E_a/E)^k$. This is in harmony with fact (k).

Summarizing what has been written above, it is clear that with the reservation already referred to in respect of (b), all of the phenomena from (a) to (f) inclusive may be correlated on the basis of an extension of the elementary theory in such a direction as to make the coefficient of absorption of the primary energy and the closely related apparent coefficient of absorption of the measured radiation increase with decrease of energy of the primaries. Moreover, all of the phenomena from (g) to (k) inclusive may be correlated on the basis of the said extension combined with the fundamental hypothesis already formulated as to the relation between primary energy and shower or burst production. It now remains to be shown how the coefficient of absorption concerned may be made to depend on the primary energy.

Realization of dependence of the coefficients of absorption upon primary energy

For purposes of continuity, we will first outline, briefly, the essentials of the elementary theory.

If n_θ represents the number of secondary rays produced per centimeter of path of the primary, inclined at zenith angle θ, and if E is the energy of the primary, the fundamentals of the theory give[16]

$$n_\theta = \alpha E \tag{1}$$

where α is a constant.

If the primaries lose energy entirely by the creation of secondaries; and, if dx is an element of path of the primary, and β is a constant,

$$-dE/dx = \beta n_\theta = \beta\alpha E, \tag{2}$$

so that $E = E_0 e^{-\beta\alpha x}$; moreover, in view of (1)

$$n_\theta = (n_\theta)_0 e^{-\beta\alpha x}, \tag{3}$$

so that both E and n_θ obey an exponential law with the same coefficient $\beta\alpha$.

We will now proceed to extend the foregoing theory by modifying (1) to the form

$$n_\theta = \alpha E^{1-\lambda}, \tag{4}$$

where λ is a constant. Under these conditions, (2) assumes the form $-dE/dx = \beta\alpha E^{1-\lambda}$, and if we define the coefficient of absorption μ_e of the energy at any point as $\mu_e = -(1/E)(dE/dx)$, we find

$$\mu_e = \beta\alpha E^{-\lambda}. \tag{5}$$

We are concerned more particularly with the measured coefficient of absorption μ_n defined as $\mu_n = -(1/n_\theta)(dn_\theta/dx)$. In view of (4),

$$\mu_n = (1-\lambda)\mu_e, \tag{6}$$

so that on the basis of the hypothesis embodied in (4), Eqs. (5) and (6) show that both μ_n and μ_e increase with decrease of energy.

A less empirical method of securing dependence of absorption coefficient upon primary energy

A similar result may be secured in another manner which has the advantage of a more direct physical significance.

Suppose that, leaving (1) unchanged, we replace (2) by

$$-dE/dx = \beta n_\theta + \gamma. \tag{7}$$

The quantity γ represents a contribution to the loss of energy per centimeter of path which is constant along the path of the primary ray. It is symbolized, for example, by such loss as is

[16] The measured intensity involves the range of the secondaries as well as n_θ. In what follows, this range is assumed constant.

represented by ionization, although we do not wish to limit it to this explanation.

Combining (1) and (7), we obtain

$$\mu_e = \beta\alpha + \gamma/E \tag{8}$$

and since, by (1), $\mu_n = \mu_e$, we have $\mu_n = \beta\alpha + \gamma/E$, which again gives an expression which causes μ_n to increase with decrease of E. Here, μ_n approximates to a constant value for high energies, this constant value being $\beta\alpha$.

The relation between the coefficients μ_n and μ_e

It is of interest to observe that if (1) be modified to

$$n_\theta = \alpha E^s \tag{9}$$

we find $\mu_n = s\mu_e$, so that if s is greater than unity, μ_n is greater than μ_e. Such a provision has an advantage in causing the ratio of the energy of the rays entering the atmosphere to the energy of the rays at sea level to be less than the ratio of the corresponding measured cosmic-ray intensities. This consequence lessens the difficulties already referred to in the matter of the asymmetric rays, concerning the entering energies as computed from the earth's magnetic field, and the sea level energies as computed from the entering energies and the coefficient of absorption.

The incorporation of (9) into the theory as represented by (7), leads to

$$\mu_e = \beta\alpha E^{s-1} + \gamma/E \quad \text{and} \quad \mu_n = s\beta\alpha E^{s-1} + s\gamma/E.$$

This expression represents a μ_n which increases with decrease of E for low values of E, but which decreases with decrease of E for high values of E.

Realization of the refinement involved in the departure from an exponential law

We now turn to the elements involved in realizing the requirement (b) in the list of requirements cited above. At first sight, the requirement of decrease of average coefficient of absorption with distance traveled seems contrary to the principle that the effective coefficient of absorption of the individual rays increases as the rays lose energy,—a principle demanded by the asymmetry effect. The difficulty is only transitory, however, for now we introduce once more the idea of a wide range of primary energies entering the atmosphere, a hypothesis which is indeed required by the latitude and directional effects. Then, although each of these rays may *soften* as a result of its passage through the atmosphere, a suitably chosen energy distribution among the entering rays will insure that the measured radiation as a whole will harden with approach to sea level. The matter may be illustrated by considering the case of two distinct energies entering the atmosphere. Let the first, denoted by subscript unity be the higher energy. For purposes of illustration we shall write, for some assigned direction $n_1 = n_{10} \exp(-\int \mu_1 dx)$. This rather artificial looking expression is adopted because it corresponds to a coefficient of absorption, defined as $-(1/n_1)(dn_1/dx)$, which is equal to μ_1 and is variable with x, if μ_1 varies with x.

In a similar manner, we write

$$n_2 = n_{20} \exp(-\int \mu_2 dx).$$

The contribution of the two types of radiation is given by

$$n = n_1 + n_2 = n_{10} \exp(-\int \mu_1 dx) + n_{20} \exp(-\int \mu_2 dx).$$

The average coefficient of absorption of the combined radiation may be defined as $\mu = -(1/n)(dn/dx)$, so that

$$\mu = (\mu_1 n_1 + \mu_2 n_2)/(n_1 + n_2).$$

To illustrate the properties of this expression it will be sufficient to remark that if at $x = 0$, i.e., at entry to the atmosphere, n_1 is small compared to n_2, μ approximates μ_2. On the other hand, at sufficiently large values of x, the quantity n_1 is large compared with the quantity n_2 on account of the required assumption that μ_2 shall be greater than μ_1. Hence, at large values of x, the coefficient μ approximates μ_1. Thus, under the condition cited we have an illustration of the fact that, while the individual quantities μ_1 and μ_2 both increase with x, the measured μ decreases from μ_2 to μ_1 with increase of x.

It is important to note that the invocation of a distribution of primary energies in the foregoing matter is on an entirely different plane from such an invocation as would be designed to give an exponential law. Here our exponential law, which represents the main story, is given as an approximation without any distribution of primary energies. In fact, to a first approxima-

tion, all primary energies give an exponential law with the same apparent coefficient of absorption.

In the foregoing discussion we have taken as the measured intensity, the intensity determined by the secondaries. We may regard each primary as accompanied by a number of secondaries equal to the product of the number emitted per centimeter of path and the range of the secondaries. It is this quantity which, in the foregoing theory, determines the contribution of a single primary to the measured intensity. The writer has given reasons for supposing that the primaries may not ionize at all until their energy has diminished to a sufficiently low value;[17] and, if such is the case, the theory as we have stated it requires no modification. If the primaries do ionize, then the contribution given, on the foregoing theory, to the number of measurable rays passing through a plane perpendicular to the path of a primary and attributable to that primary, should be increased by unity. This does not disturb the essentials of the theory, however.

It is of interest to note that if q is the number of secondaries produced per centimeter of path by a primary, and if each secondary has an energy of 10^8 electron volts, the loss of energy per centimeter of path would be $q\times 10^8$. On the other hand, the loss of energy per centimeter of path at a place where the primary energy is E, is, according to the elementary theory, equal to μE, where μ is the absorption coefficient. Estimating all lengths in terms of centimeters of air compressed to the density of water, we have $\mu=0.005$. Hence, $q\times 10^8=0.005E$. If E is of the order of 10^{10} electron volts, $q=0.5$. The range of 10^8-volt secondaries is of the order 20 cm in air compressed to the density of water. Hence the number of electrons accompanying each primary at the place where the primary energy is 10^{10} volts is of the order $20\times 0.5=10$. The question of whether the primary is, or is not, added becomes therefore of small importance; although the importance is increased for small primary energies.

Any difficulty concerned with the participation of the primary in direct ionization may be removed by a modification of the theory in which what we have above regarded as the primaries are really photons in their journey through the atmosphere. We must suppose that these photons receive their energies and their directional characteristics in their creation from the real charged particle primaries by impact of the latter with atoms of air in the higher regions of the atmosphere. If then we impute to the photons the same characteristics of shower production, energy loss, etc., as we have imputed to the primaries in the foregoing discussion, the whole theory already given follows again in all its essential details. As the photons lose energy, their frequencies of course change.

It is not my purpose to attempt to fix too definitely at this stage, the exact forms of the details of the various elements of the corpuscular theory here presented. It will suffice to say that, within the general spirit of the ideas outlined in the elementary form of the theory, it is possible to make modifications which will include all the experimental facts concerned with absorption in the atmosphere, and with the latitude and directional effects. By the further hypothesis already cited, to the effect that, in the case of the heavy atom elements, frequency of shower production and the like depend upon a higher power of the primary energy than the first, we are able to correlate with the theory the experiments already cited in relation to such phenomena, together with a number of other experiments relating shower production to altitude, and to the characteristics of the primary rays as determined by their direction, or by their behavior in the matter of asymmetry.

[17] W. F. G. Swann, Phys. Rev. **43**, 945 (1933); also Phys. Rev. **46**, 432 (1934).

The Effect of Primary Cosmic-Ray Energy Upon Burst Production[1]

W. F. G. SWANN AND D. B. COWIE, *Bartol Research Foundation of the Franklin Institute*

(Received July 29, 1935)

The fact that the intensity of burst and shower production increases with altitude much more rapidly than does the cosmic-radiation intensity itself lead one of us to the view that the intensity of burst production was a rapidly increasing function of the energy of the primary cosmic rays. If such is the case, burst production per unit intensity of primary, by primary rays which are limited to a vertical direction, should be much larger than the corresponding quantity for primary rays limited to directions in the neighborhood of 45 degrees, since the latter rays have traveled a much greater thickness of atmosphere. To test this conclusion we set up an apparatus comprising a one-inch thick iron sphere suitably arranged as a burst-measuring ionization chamber. One set of counters was placed vertically above and another was placed vertically below the center. The two were used as a double coincidence set. Coincidences between the counter discharges and the bursts produced serve to indicate which bursts were produced by the vertical rays determined by the counter system. An exactly similar pair of counters arranged at 45 degrees to the vertical gave the information for this direction also. The experiments show that while over a period of 300 hours the numbers of counts obtained by the vertical and 45 degree counters were in the ratio of 1.5 to 1, the corresponding numbers of bursts (involving more than 2×10^6 ions) were in the ratio of 10 to 1, which result confirms the conclusion cited above. It is possible to calculate from the experiments of C. G. and D. D. Montgomery at sea level and at Pike's Peak the magnitude of the effect to be expected in the present experiment on the basis of the general ideas formulated as controlling the phenomenon. The agreement obtained is within the limits of accuracy of the experiments.

THE experiments of C. G. and D. D. Montgomery[2] have shown that the rate of production of bursts in lead increases by a factor of twenty-five between sea level and the altitude of Pike's Peak, whereas the cosmic-ray intensity increases by a factor of only five. Similar results have been obtained by R. D. Bennett, G. S. Brown and H. A. Rahmel.[3] Results in harmony with these conclusions but for showers of smaller size have also been obtained by T. H. Johnson[4] and by B. Rossi and S. de Benedetti.[5]

One of us[6] has emphasized the significance of these results as calling for a dependence of the *quality* of the radiation upon the altitude, and has evolved a theory of the phenomenon according to which the rate of production of bursts in elements of high atomic weight depends upon a power of the primary energy higher than the first, while the measured cosmic-ray intensity depends approximately upon the first power of the energy. If this conclusion is correct, it follows that primary rays coming in a direction inclined to the vertical should be less efficient in burst production than should vertical rays since the inclined rays have traveled so much further in the atmosphere; and the purpose of the present investigation is to test this question.

The apparatus used is represented diagrammatically in Fig. 1. In its essentials, its plan and scheme of operation is as follows: *A* is an iron sphere about 14 liters capacity, with walls 1 inch thick and filled with nitrogen to a pressure of 200 lbs. per square inch. It is provided with a system of concentric electrodes, one set of which

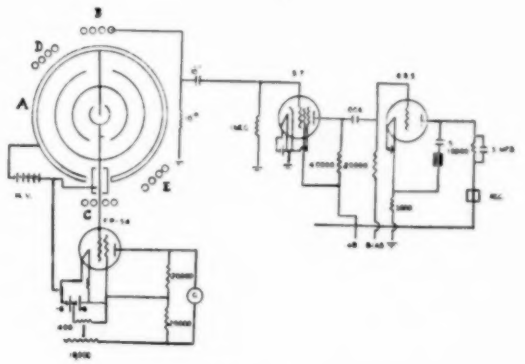

FIG. 1.

[1] Presented at the Washington Meeting of the Am. Phys. Soc., 1935.
[2] C. G. and D. D. Montgomery, Phys. Rev. **47**, 429 (1935).
[3] R. D. Bennett, G. S. Brown, and H. A. Rahmel, Phys. Rev. **47**, 339 (1935).
[4] T. H. Johnson, Phys. Rev. **45**, 569 (1934).
[5] B. Rossi and S. de Benedetti, Ricerca Scient. **5**, 1 (1934).
[6] W. F. G. Swann, Phys. Rev. **46**, 828 (1934).

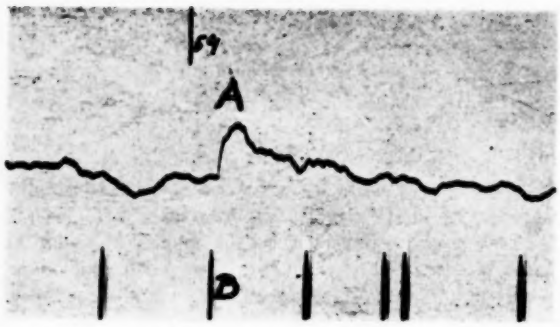

FIG. 2.

forms part of the insulated system, the other set forming, electrically, a unit with the sphere. Bursts generated in the walls of the iron sphere send their rays into the nitrogen, producing ions which by operation of a potential difference of 800 volts between the two systems of electrodes are driven to those electrodes. The purpose of the concentric system is to provide a short time of collection of ions, and so provide for the greatest discrimination between real bursts and apparent bursts resulting from statistical fluctuations. The measurement of the spurts of ions collected by the central insulated system was effected through a FP–54 Pliotron connected to that system and operating finally a d'Arsonval galvanometer of 5-second period. A vertical illuminated line from the galvanometer fell across a horizontal slit of a camera containing photographic paper moving at the rate of 1/10 mm per second, so that the occurrence of a burst was represented by a displacement of the photographic image such as is represented at *A* in Fig. 2.

In addition to the above-described system, there was, independently, a system of Geiger-Müller counters. Two sets of counters, *B* and *C*, Fig. 1, operated as a double coincidence set, and recorded the primary cosmic rays or their representatives[7] coming within angles determined by the areas and distance apart of the counters. The area of the sets *B* and *C* was in each case 80 square centimeters, and the distance between them was 52 cm so that the angle subtended by one set at the center of the other was about 10 degrees. A similar set of counters *D* and *E* served a corresponding purpose for the primary cosmic rays falling within an equal angle with axis of symmetry inclined at 45 degrees to the vertical. The details of the counter circuits are sufficiently clear from the figure.

The coincident counter discharges were caused to operate a lamp which illuminated the slit of the camera, and so appeared upon the record which carried the galvanometer trace. The records from the vertical set of counters were caused to be distinguished from the 45° set by arranging that different lengths of the camera slit were illuminated in the two cases. Fig. 3 is an actual picture of the apparatus. The significance of its parts will be clear from the legend attached.

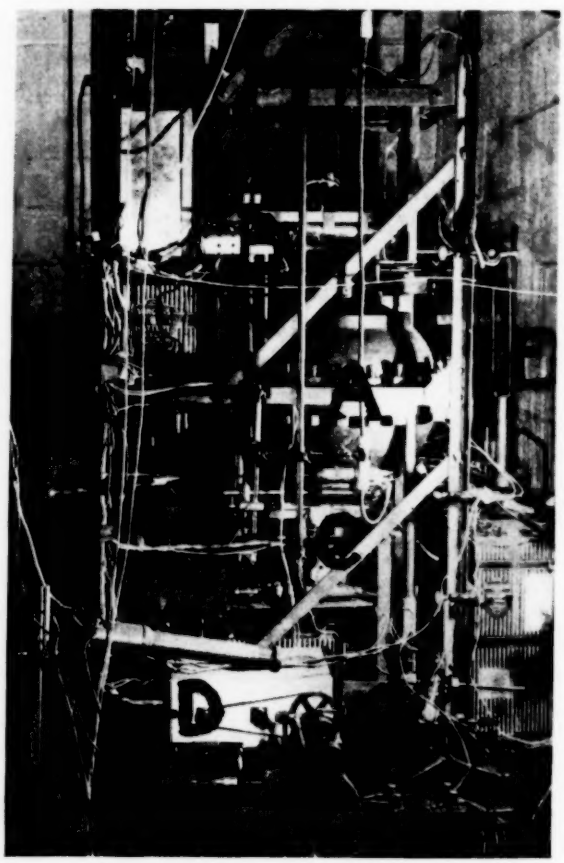

FIG. 3. *A* is the sphere. The upper sets of counters are shown near *B*, and the lower set near *C*. *D* is the camera. The main galvanometer is not shown. *E* is a subsidiary galvanometer for visual observations.

[7] According to the views set forth in the paper cited under [6] the actual phenomena observed in the counters are, for the most part, those caused by secondaries produced by and accompanying the primaries.

The ultimate record thus contained a galvanometer trace with burst deflections upon it, and it contained two sets of counter discharges, a set corresponding to discharges of the counters arranged symmetrically to the vertical, and a set corresponding to the discharges of the counters arranged symmetrically to the 45° line. Fig. 2, in addition to showing the burst at A, shows, coincident with it, a counter discharge indicated by the line B, and corresponding in this case to the vertical counters.

The record contained, of course, many traces of counter discharges which were not accompanied by bursts. The general waviness of the galvanometer trace is the result of statistical fluctuation produced by the cosmic-ray ionization in the sphere.

The plan was to list the following quantities for the interval corresponding to the experiment.

N_v the total number of discharges of the vertical counters during the interval.

N_f the total number of discharges of the 45-degree counters during the interval.

N_{vs} the total number of cases of coincidence of a burst with one of the N_v counter discharges.

N_{vf} the total number of cases of coincidence of a burst with one of the N_f counter discharges.

Such a list is contained in Table I, in which the

TABLE I.

N_v	N_f	N_{vs}	N_{fs}	N_{vs}/N_{fs}	N_{vs}/N_v	N_{fs}/N_f
3563	2262	70	7	10	0.0197	0.0031

galvanometer displacements listed as bursts are confined to those corresponding to the collection of more than 2.0×10^6 ions, this being the limit which is calculated for the size of burst which, taking into account the time of collection of the ions (0.2 second), and the cosmic-ray ionization, can be distinguished satisfactorily from an apparent burst produced by cosmic-ray statistical fluctuations.

According to a view which represented the counters as measuring numbers of primary cosmic rays or their representatives, the quantities N_{vs}/N_v and N_{fs}/N_f could be regarded, respectively, as comparative measurements of the efficiency of production of bursts by a vertical and a 45° ray. A basis of representation more in line with the principles formulated in the paper cited,[6] however, would view the number of primary rays per square centimeter per unit solid angle as equal for the vertical and for the 45° directions, the difference between the number of counter discharges for the two directions being concerned merely with the difference of the efficiency of the vertical and 45° rays in producing long range secondaries in air, and in the present case, also in the walls of the room. On this view the quantities N_{vs} and N_{fs} represent the relative efficiencies of vertical and 45° rays. Whether we like this view, which seems to be the only one having logical meaning, or the more naïve view which regards N_{vs}/N_v and N_{fs}/N_f as the relative efficiencies, it will be seen that, in line with the views already cited, the vertical rays are much more efficient than those which enter the apparatus at 45° to the vertical and which have consequently traveled, in the atmosphere, a distance which is greater than that for the vertical rays in the ratio of 1.4 to unity.

It should be remembered that there were in the interval six cases where there was a coincidence between the discharges of both counter pairs and also between these discharges and the occurrence of a burst as recorded by the galvanometer. The probability of a coincidence between the vertical and 45° counter sets is negligible unless produced by a burst or large shower originating outside the sphere. The inference is that these six cases are representative of phenomena of this type, the probability of the occurrence of the phenomenon being augmented by the burst particles produced in the sphere and being responsible for the observed burst itself. On this view the six cases are representative of phenomena which should not be included in the main story of the investigation. However, even if we should include them, the conclusion as to the 45° rays in relation to the vertical rays remains, although the magnitude of the difference becomes reduced.

Incidentally, and quite apart from any theory of the matter, it may be remembered that these experiments afford a reason for the oft-stated conclusion to the effect that burst particles travel for the most part vertically downwards. At first sight such a result would be contrary to all that might logically be expected, since there is no reason to expect anything but symmetry of ejection of burst particles in relation to the

direction of the primary rays which produce them. The normal to the earth's surface has no primary significance in the matter; and, if the inclined primaries produce bursts in amount proportional to their number, it is very difficult to see how the supposed verticality of burst particle projection, or symmetry about the vertical, could be accounted for. Once one recognizes the tremendous diminution of efficiency of burst production by the primaries with angular departure from the vertical, however, the whole matter becomes satisfactorily explained.

It may be of interest to invoke the ideas already cited as to the relation between the results of this experiment and the results obtained by the Montgomerys in what is, at first sight, an entirely different type of experiment. Only a crude quantitative comparison is possible, partly on account of the fact that the number of bursts obtained for the 45° direction in the present experiment is so small as to form a rather inadequate representative of the true average number for the interval, and partly on account of the fact that, in the experiments of the Montgomerys, bursts produced by rays from all directions were counted. Then, the investigation here reported concerns itself with a comparison of the efficiency of burst production by rays whose energy is less than that of the rays reaching the earth's surface normally, with the efficiency for the normal rays, while the experiment of the Montgomerys concerns itself with a comparison of the efficiency of burst production by rays whose energy is, on the average, greater than that of the rays reaching the earth's surface with the efficiency of production for the normal rays.

However, with these reservations, a comparison may be made as follows: The theory cited[6] gives the coefficient of absorption of energy as equal to that of the measured intensity of the cosmic radiation, so that the primary energy at the summit of Pike's Peak should be five times that at the earth's surface. Since the atmosphere below the summit of Pike's Peak corresponds to 0.4 of the vertical height of the homogeneous atmosphere, if μ is the coefficient of absorption of the energy in the homogeneous atmosphere of total height H, we have $e^{0.4\mu H}=5$, from which $\mu H=4$. It follows[8] from this that the ratio of the energy for the 45° rays in the present experiment to that for the vertical rays is $e^{-0.41\times 4}=0.2$. Since, according to the experiments of the Montgomerys, the rate of burst production increases proportionally to the square of the measured intensity, and so proportionally to the square of the energy, we should expect the number of bursts produced by the 45° rays to be $(0.2)^2=0.04$ of the number for the vertical rays. Within the limits of the experimental errors, statistical errors and assumptions, this results in good harmony with the value 0.1 quoted for N_{fs}/N_{vs} in Table I.

It is possible to eliminate from the above comparison of the present experiments with those of the Montgomerys the elements of the theory outlined in the paper cited,[6] and to base everything upon the empirical comparison between the rate of production of bursts and the measured intensity of cosmic radiation. The arguments and calculations are exactly similar to those just given with the elimination of the introduction of the primary energy into the matter. Such an argument lends confidence to the experimental data regardless of any theory; but the theory becomes necessary for the importation of physical significance into either of the two sets of experiments compared.

The writers wish to express their appreciation to the American Philosophical Society for a grant, part of which was used in furthering the foregoing investigation.

[8] We make the approximate assumption that the increase with altitude of the ionization integrated for rays of all directions is exponential with the same absorption coefficient as for a single direction.

Scattering of Slow Neutrons

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(Received August 1, 1935)

With the radioactivity produced in a silver foil as a detector of neutrons, the scattering of slow neutrons by the metals Fe, Cu, Pb, Sn and Hg has been investigated. Curves showing percentage scattering as a function of thickness are given, from which the relative cross section for scattering has been calculated.

INTRODUCTION

DUNNING, Pegram, Fink and Mitchell[1] and Amaldi, D'Agostino, Fermi, Pontecorvo, Rasetti and Segrè[2] have investigated the absorption of slow neutrons by various metals. Dunning[3] has also measured the absorption of fast neutrons by a large number of substances. In these experiments, an almost parallel beam of neutrons was incident on an ionization chamber containing hydrogen, or in the later experiments lithium, as a detector. The interposition of various metals caused a decrease in the number of neutrons entering the chamber. The number was found to decrease exponentially with the thickness of the absorber and from these data an absorption coefficient and hence a cross section for absorption could be obtained. In the experiments with slow neutrons, a sphere of paraffin, 6 cm in diameter, surrounded the neutron source, and the absorption of the slow neutrons was measured in the same manner as before. In the experiments of Fermi and his collaborators, however, the radioactivity produced by neutrons in a silver or rhodium sheet served as an indicator of the number of neutrons. The absorption was then obtained by noting the decrease in the activity of the silver or rhodium sample as a function of the thickness of absorber.

Dunning found a monatonic increase in cross section with increasing atomic weight of scatterer in the case of fast neutrons. For the slow neutrons, however, certain metals, notably cadmium and mercury, showed absorption cross sections considerably higher than they showed for fast neutrons. In the case of elements showing small cross sections, it was generally supposed that the absorption was due largely to scattering of neutrons out of the beam rather than to true absorption. The large cross sections to slow neutrons exhibited by some substances was attributed to capture of the neutrons by these metals.

Up to the present there have been very little data obtained for the scattering of neutrons by various metals. Indeed, it is difficult to devise an experiment for this purpose in which one is sure that multiple scattering and absorption are not playing a predominant role. The purpose of this paper is to report some experiments which throw some light on this problem and from which can be obtained relative scattering cross sections for some metals. A preliminary report on the scattering by iron and copper appeared at an earlier date,[4] and the present work confirms and amplifies this.

APPARATUS AND METHOD

The apparatus, shown in Fig. 1, consisted of a cylindrical bucket filled with paraffin, in which was placed a bulb, *S*, containing radon (250 millicuries to 60 millicuries) and beryllium. After passing through approximately 6 cm of paraffin, the neutrons struck a silver foil, 6×10 cm, and then were scattered from blocks of metal, the same size as the foil, placed above it. The scattering was measured by observing the increase in the radioactivity of the silver foil caused by the presence of various thicknesses of scatterer.

The activity of the foil was measured with the help of a Geiger-Müller tube counter. The

[1] J. R. Dunning, G. B. Pegram, G. A. Fink and D. P. Mitchell, Phys. Rev. **47**, 416 (1935).
[2] E. Amaldi, O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti and E. Segrè, Proc. Roy. Soc. **A149**, 522 (1935).
[3] J. R. Dunning, Phys. Rev. **45**, 586 (1934).
[4] A. C. G. Mitchell and E. J. Murphy, Phys. Rev. **47**, 881 (1935).

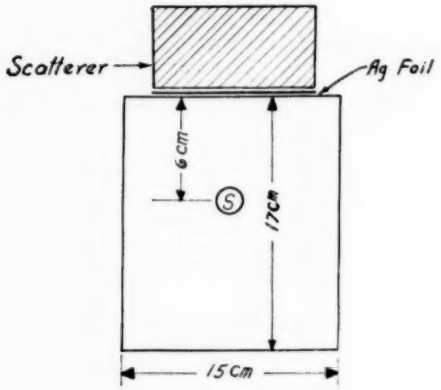

FIG. 1. Apparatus.

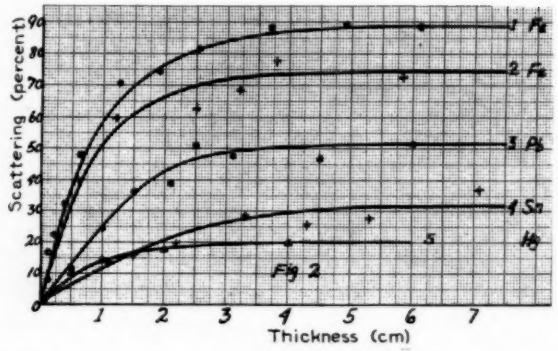

FIG. 2. Scattering of slow neutrons by Fe, Pb, Sn and Hg.

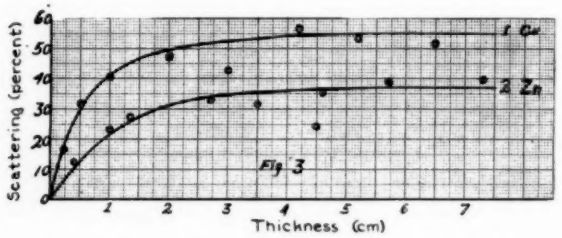

FIG. 3. Scattering of slow neutrons by Cu and Zn.

counters used in these experiments were made of thin-walled aluminum tubing and were filled with either argon or air. The potential was supplied to the case by a stabilized voltage source which kept the voltage constant to within 0.1 percent. The impulses from the counter were amplified and then fed into a thyratron "scale of two counter."

The usual procedure in carrying out the experiment was to irradiate the silver foil, with no scatterer present, for six minutes. The foil was then removed and wrapped around the tube counter. Counting was begun one minute after removing the foil from the source and continued until the end of the fifth minute. The total count in this interval, minus the natural background of the counter, was then recorded. In the scattering experiments blocks of metal of various thicknesses were placed directly above the foil, which was then irradiated and counted in the same manner as before. The percentage scattering was then obtained by subtracting the activity of the foil with no scatterer present, corrected for radon decay, from that with scatterer present and dividing by the activity of the foil alone. In this way a curve could be plotted in which the percentage scattering appeared as ordinate and the thickness of scatterer as abscissa.

RESULTS

The results of the experiments are shown in Figs. 2 and 3. All curves except curve 2 of Fig. 2 were taken under identical conditions. It should be noted that all the curves start out nearly linearly from the origin and then bend off gradually to a region in which the scattering is independent of thickness. This latter region is difficult to interpret since multiple scattering and absorption are probably playing a large role. On the other hand, in the initial part of the curves it is reasonable to suppose that single scattering is predominant, since the scattering is proportional to the thickness.

If single scattering obtains, the slope of the curves as they come out of the origin should be given by $N\sigma^2 c(\theta)$, where N is the number of atoms per cc, σ^2 the collision cross section for scattering, and $c(\theta)$ is a quantity which gives the fraction of neutrons which are scattered through an angle θ sufficiently great so that they will return and strike the foil. This quantity will depend on the angular scattering function, $f(\theta)$, which is supposed to be a constant for slow neutrons,[5] and the angle which the oncoming neutrons make with a plane through the detecting foil. This latter is not definitely known, as the neutrons probably have all directions

[5] H. A. Bethe and R. Peierls, Proc. Roy. Soc. **A149**, 176 (1935).

between nearly 0° and 180° with a line drawn in this plane parallel to the long direction of the foil. Experiments, in which the activity of the silver foil was measured as a function of the distance from the top of the paraffin, showed that the neutron beam was in effect not parallel. Furthermore, experiments were performed in which the foil was placed at 2.5 cm and 4.5 cm, respectively, from the top of the paraffin and scattering curves taken for iron, with the scatterer placed directly above the foil. The slopes of the curves became smaller as the distance from top of paraffin to foil increased. This is to be expected since the fraction of scattered neutrons which return to the foil becomes less as the angular divergence of the beam decreases. The geometry was, however, not simple enough to allow one to calculate $c(\theta)$. Since the same geometry was used for all scattering curves shown in Figs. 2 and 3, it will be sufficient to put $c(\theta)=1$ and calculate the *relative* scattering cross sections. The values thus obtained are given in Table I, along with the absorption cross sections given by Dunning and collaborators.[6]

It will be seen from the table that, with the exception of mercury, the scattering cross sections are of the same order of magnitude and have the same relative size for the elements iron to tin as the observed absorption cross sections

The case of mercury is of particular interest since the absorption cross section has been shown to be extremely large by both Dunning and Fermi. The scattering experiments on mercury were carried out on the liquid, which was contained in a "tin" box, the scattering from which was previously found to be negligible. It will be seen from curve 5 of Fig. 2 that the scattering curve rises very slowly and that the total scattering is never greater than 20 percent.

TABLE I. *Relative scattering cross sections for slow neutrons.*

METAL	CROSS SECTION	
	Scattering	Absorption
Fe	9.9	12.0
Pb	7.2	8.6
Cu	7.7	7.5
Zn	3.4	4.7
Sn	3.8	4.0
Hg	4.4	380

[6] J. R. Dunning, G. B. Pegram, G. A. Fink and D. P. Mitchell, Phys. Rev. **48**, 265 (1935).

The curve indicates that the scattering cross section is not anomalously large and, on account of the small scattering at thicknesses of 3 to 4 cm, that the absorption cross section is relatively big. This is in agreement with the idea that the large absorption cross section is due to capture.

Some experiments have been performed which were designed to show whether the velocity distribution of the neutrons is changed on scattering from various materials. For example, if some of the faster neutrons are slowed down on being scattered by a metal, they might cause a greater activity in the silver than if their velocity had not been changed. It was first ascertained that a sheet of cadmium 0.25 mm thick, placed between the paraffin and foil, decreased the total count given by the foil (no scatterer present) from 2600 in four minutes to 800. An additional 0.25 mm sheet only reduced the count to 700. Measurements were then made with a 0.25 mm cadmium sheet between the neutron source and foil, and readings were taken with the scatterer in place with and without a second cadmium sheet 0.25 mm thick between the silver foil and the scatterer. Within the limits of error the results showed that the count was the same with or without the second cadmium sheet for the scatterers iron, tin, lead and copper. In the case of zinc a somewhat smaller count was obtained with the second sheet of cadmium in place than without it. The effect was small, however, and lay just outside the limit of error. If the scatterers had been very effective in slowing down neutrons of the velocity range used, a considerable decrease should have been detected when the second cadmium sheet was in place, since it would have been very effective in removing the slower neutrons from the scattered beam. No large effect was found, however, and one should therefore conclude that, for neutrons that have passed through 6 cm paraffin, the metals investigated, with the exception of zinc, do not slow the neutrons down further.

Finally, a scattering curve for iron was taken in which the neutrons, issuing from the paraffin, had passed through a sheet of cadmium 0.65 mm thick, placed between the paraffin and the silver foil. The scatterer was placed above the foil in the usual manner. The results are shown in

curve 2 of Fig. 2. The neutrons striking the scatterer are presumably faster than if no cadmium had been present. It will be seen from the curve that the scattering from iron is less for these neutrons than for those which have not passed through cadmium. The cross section, calculated from the curve, is 8.1×10^{-24} cm².

We are indebted to Mr. Lawrence M. Langer for help in taking some of the readings and to Dr. C. B. Braestrup of the Physical Laboratory of the Department of Hospitals of the City of New York for many favors. We also wish to acknowledge our indebtedness to the American Association for the Advancement of Science for a grant to one of us (A. C. G. M.) with the aid of which apparatus has been purchased.

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The Spectrum of the Zinc Arc in Vacuum

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(Received July 10, 1935)

Sixty lines in the spectrum of the vacuum zinc arc have been observed in the wave-length range 2178A to 7799A. All known solar zinc lines, including two not hitherto listed, are included. A suitable source for obtaining weak lines in vacuum is described. The stronger lines of the following elements were observed: Pb, Cu, Cd, Ag, Sn, Na, K, Rb, Cs, Sr, Be. The observations were made by means of the F and P interferometer, and by various gratings and prisms.

THE spectrum of the zinc arc was observed with a view to obtaining accurate vacuum wave-lengths of all those lines which are now, or might soon be, of astrophysical importance. This object has perhaps been attained, since precise values have been measured for the lines which have been identified as zinc in the *Rowland Revision*.[1] Two additional solar lines, both weak, are probably due at least in part to zinc. These are λ4292A and λ7799A.

The derivation of precise values of the atomic levels of an element usually makes it possible to compute accurate wave-lengths of lines which cannot be easily observed, either because the lines are faint, or because they lie in an inaccessible region of the spectrum. In the case of our work on zinc, only two such lines can be computed; λ1404A and λ1457A. The combinations of the low singlet S with the odd triplet P terms give rise to lines in the Schuman region; these are undoubtedly quite faint. Other possible combinations give lines in the far infrared.

The source of the zinc spectrum of wave-length less than 3700A was an arc in vacuum between brass electrodes, operated at 4 amperes. In the longer region, special brasses containing up to 80 percent zinc[2] were used in addition to commercial brass. Whatever the initial percentage of zinc, after the arc had run five minutes the tips of the electrodes were reduced to that alloy which remains stable at the operating temperature, and this is very low in zinc.

The strong lines of zinc can be observed in sharp condition and with reasonable exposure times by using carbon electrodes which have been soaked in a solution of a zinc salt. To obtain satisfactory sharpness, the amperage must be low. Zinc sulphate packed into a thin-walled copper or silver tube proved to be a fairly satisfactory source. For the weak lines, requiring long exposure at high current, the most satisfactory source was a pool of molten zinc held in a large brass cup, and an upper electrode of sterling silver. The use of copper as an upper electrode caused the zinc to oxidize more rapidly than was the case when silver was used; this made it

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[1] St. John, Moore, Ware, Adams, and Babcock, *Revision of Rowland's Preliminary Table of Solar Spectrum Wavelengths* (1928).

[2] Kindly alloyed for us by Federated Metals Corporation.

TABLE I. *Wave-lengths in the zinc arc in vacuum.*

λ (Air)	ν (Vacuum)	Terms	Int.	p.e.	Instrument
1404.118*	71219.077	$4^1S_0-7^1P_1^0$			
1457.572*	68607.256	$4^1S_0-6^1P_1^0$			
2138.56 –	46745.6 –	$4^1S_0-4^1P_1^0$	100R	D	P
2312.72 –	43225.8 –	Zinc II	3	D	P
2502.001	39955.97	Zinc II	4	A	G3, P
2515.807**	39736.72	$4^3P_2^0-7^3D_3$	1	D	I
2557.958	39081.97	Zinc II	20	D	I
2569.871	38900.81	$4^3P_0^0-6^3D_1$	8	B	I
2582.440	38711.49	$4^3P_1^0-6^3D_2$	7	C	G3
2582.487	38710.79	$4^3P_1^0-6^3D_1$	1	D	G3
2608.558	38323.92	$4^3P_2^0-6^3D_3$	30	B	G3, I
2608.640	38322.72	$4^3P_2^0-6^3D_2$	5	D	G3
2670.530	37434.64	$4^3P_0^0-7^3S_1$	2	C	G2, I
2684.161	37244.55	$4^3P_1^0-7^3S_1$	6	C	I
2712.488	36855.62	$4^3P_2^0-7^3S_1$	10	B	I
2756.452	36267.82	$4^3P_0^0-5^3D_1$	60	A	I
2770.865	36079.18	$4^3P_1^0-5^3D_2$	80	A	I
2770.984	36077.63	$4^3P_1^0-5^3D_1$	25	C	G2
2800.869	35692.71	$4^3P_2^0-5^3D_3$	80	C	G2
2801.056	35690.33	$4^3P_2^0-5^3D_2$	15	B	G2
2801.167	35688.91	$4^3P_2^0-5^3D_1$	2	D	G2
3018.352	33121.04	$4^3P_0^0-6^3S_1$	30	B	I
3035.781	32930.87	$4^3P_1^0-6^3S_1$	35	B	G2, I
3072.062	32542.00	$4^3P_2^0-6^3S_1$	70	B	I
3075.901	32501.39	$4^1S_0-4^3P_1^0$	90	B	I
3282.333	30457.39	$4^3P_0^0-4^3D_1$	100	B	G2, I
3302.588	30270.60	$4^3P_1^0-4^3D_2$	150	C	G2
3302.941	30267.36	$4^3P_1^0-4^3D_1$	125	C	G2
3345.020	29886.63	$4^3P_2^0-4^3D_3$	150	D	G2
3345.572	29881.69	$4^3P_2^0-4^3D_2$	100	D	G2
3345.934	29878.46	$4^3P_2^0-4^3D_1$	30	B	G2
3799.002	26315.26	$4^1P_1^0-9^1S_0$	3	D	G1
3883.340	25743.76	$4^1P_1^0-7^1D_2$	3	D	G1
3965.432	25210.83	$4^1P_1^0-8^1S_0$	15	D	G1
4101.665	24373.49	Indium?	3	D	G1
4113.210	24305.08	$4^1P_1^0-6^1D_2$	12	D	G1
4292.885	23287.83	$4^3P_1^0-5^1S_0$	8	A	I
4298.327	23258.35	$4^1P_1^0-7^1S_0$	6	B	I
4629.814	21593.113	$4^1P_1^0-5^1D_2$	12	A	I
4680.138	21360.933	$4^3P_0^0-5^3S_1$	45	A	I
4722.159	21170.851	$4^3P_1^0-5^3S_1$	75	A	I
4810.534	20781.924	$4^3P_2^0-5^3S_1$	65	A	I
4911.664	20354.03	Zinc II	6	C	G1, I
4924.043	20302.86	Zinc II	6	D	I
5068.655	19723.62	$5^3S_1-9^3P_2^0$	2	D	G1
5069.577	19720.31	$5^3S_1-9^3P_1^0$	1	D	G1
5181.995	19292.231	$4^1P_1^0-6^1S_0$	30	A	I
5308.648	18831.96	$5^3S_1-8^3P_2^0$	3	D	G1
5310.241	18826.32	$5^3S_1-8^3P_1^0$	2	D	G1
5311.02 –	18823.6 –	$5^3S_1-8^3P_0^0$	1	D	G1
5772.102	17319.92	$5^3S_1-7^3P_2^0$	10	D	I
5775.501	17309.73	$5^3S_1-7^3P_1^0$	6	D	I
5777.112	17304.90	$5^3S_1-7^3P_0^0$	3	D	G1
5894.351	16960.71	Zinc II	2	D	I
6237.891	16026.64	$4^1P_1^0-4^3D_2$	5	B	I
6239.182	16023.32	$4^1P_1^0-4^3D_1$	1	C	I
6362.347	15713.136	$4^1P_1^0-4^1D_2$	100	A	I
6479.155	15429.86	$5^1S_0-7^1P_1^0$	10	B	I
6928.319	14429.543	$5^3S_1-6^3P_2^0$	10	A	I
6938.472	14408.428	$5^3S_1-6^3P_1^0$	6	C	I
6943.202	14398.613	$5^3S_1-6^3P_0^0$	2	A	I
7799.365	12818.036	$5^1S_0-6^1P_1^0$	1	B	I

* Reciprocal of the wave number.

** Classification doubtful.

necessary to open the lamp house frequently to clear away the oxide which forms around the arc. The silver electrode was scarcely consumed at all. The lines were quite sharp in the silver-zinc source.

Some of the lines were measured by means of a prism spectrograph only, others by means of a grating; these are indicated by P or G in the last column of each table. The number following the G indicates the order. The symbol I in the last column means that the measurement was made by means of an interferometer. For wave-lengths shorter than 3570A a separation of 3.75 mm was used; from 3572A to 4200A, separations of 3.75 mm and 8.00 mm were used. From 4292A to 7800A, separations of 3 to 20 mm were used; some lines would not stand the highest resolving power under the conditions of operation.

In the shorter region, the copper lines, and some iron lines occurring as impurities, were used to determine the thickness of the interferometer. In the region longer than 4200A the lines were compared with neon by simultaneous exposure.

The term system of zinc is quite simple. The active electrons are but two in number, and in every case one of these is 4*s*. The terms are numbered in such a manner that the electron configuration is found by adding to 4*s* an electron of the same number and letter as those of the term. Thus 5^1S_0 and 5^3S_1 have the electron configuration $4s5s$: $4^1P_1^0$ and $4^3P^0_{0,\,1,\,2}$ have the configuration $4s4p$.

The strong lines of zinc, and many of the weak ones, are as nearly sharp as can be estimated under the observing conditions. Although the

TABLE II. *Relative term values in the spectrum of zinc I.*
(Derived from wave-lengths in Table I.)

4^1S_0	0.000	4^1D_2	62458.51	5^3D_1	68579.13
5^1S_0	55789.220	5^1D_2	68338.48	5^3D_2	68580.60
6^1S_0	66037.60	6^1D_2	71050.45	5^3D_3	68583.03
7^1S_0	70003.72	7^1D_2	72489.13		
8^1S_0	71956.20			6^3D_1	71212.13
9^1S_0	73060.63	4^3D_1	62768.75	6^3D_2	71212.90
		4^3D_2	62772.00	6^3D_3	71214.24
5^3S_1	53672.241	4^3D_3	62776.95		
6^3S_1	65432.32				
7^3S_1	69745.94				
$4^1P_1^0$	46745.37	$4^3P_0^0$	32311.308	$8^3P_0^0$	72495.8 –
$6^1P_1^0$	68607.26	$4^3P_1^0$	32501.390	$8^3P_1^0$	72498.56
$7^1P_1^0$	71219.08	$4^3P_2^0$	32890.317	$8^3P_2^0$	72504.20
		$6^3P_0^0$	68070.854	$9^3P_1^0$	73392.27
		$6^3P_1^0$	68080.669	$9^3P_2^0$	73395.86
		$6^3P_2^0$	68101.784		
		$7^3P_0^0$	70977.14		
		$7^3P_1^0$	70981.97		
		$7^3P_2^0$	70992.16		

TABLE III. *Wave-lengths of various elements, vacuum arc.*

λ (air)	(vac.)	Int.	p.e.	Instrument
	A. LEAD			
2169.994	46068.57	2	B	P
2203.528	45367.56	15	B	P
2237.421	44680.40	3	C	P
2332.43 −	42860.6 −	5	D	P
2388.78 −	41849.6 −	3	D	P
2393.795	41761.93	30	A	G3, I
2399.58 −	41661.3 −	4	D	P
2401.945	41620.25	25	A	I
2411.735	41451.31	15	C	G3
2443.830	40906.97	8	A	I
2446.184	40867.61	20	B	I
2476.381	40369.32	60	A	G3, I
2577.266	38789.20	30	B	G3, I
2613.657	38249.16	40	B	G3, I
2614.178	38241.54	80	B	G3, I
2628.263	38036.61	4	C	I
2663.158	37538.26	90	A	I
2802.000	35678.30	60	B	I
2823.189	35410.54	30	A	I
2833.067	35287.08	50	A	G2, I
2873.316	34792.81	70	A	I
3572.734	27981.81	60	A	I
3639.568	27467.99	90	A	I
3671.494	27229.14	20	A	I
3683.469	27140.62	90	A	I
3739.940	26730.82	50	A	I
4019.636	24870.87	6	A	I
4057.812	24636.89	100	A	I
4062.138	24610.65	20	A	I
4168.035	23985.38	4	C	I
5005.427	19972.76	4	C	I
5201.444	19220.09	1	C	I
6001.884	16656.83	2	D	I
	B. COPPER			
3654.243*	27357.68	2	B	I
3860.472*	25896.25	3	B	I
4480.354	22313.424	6	A	I
4509.377	22169.814	4	A	I
4530.787	22065.054	6	A	I
4651.160	21494.160	8	A	I
4697.522	21281.88	4	D	I
4704.606	21249.836	6	B	I
5016.613	19928.227	3	A	I
5105.541	19581.121	8	B	I
5111.918	19556.695	2	A	I
5153.233	19399.906	8	B	I
5212.780*	19178.30	1	D	I
5218.204	19158.362	10	A	I
5220.073	19151.502	6	B	I
5292.518	18889.357	4	A	I
5352.666*	18677.10	2	D	I
5360.030*	18651.439	1	B	I
5463.094*	18299.57	2	D	I
5554.935*	17997.03	3	C	I
5631.670*	17751.81	1	D	I
5700.244	17538.254	6	B	I
5732.325*	17440.10	1	C	I
5782.133	17289.873	8	A	I
7933.130	12601.904	10	B	I
8092.639	12353.517	10	A	I
	C. CADMIUM			
2144.382	46618.74	15	D	P
2265.017	44136.09	70	D	G3
2288.018	43692.44	80	D	G3
2312.57 −	43228.6 −	5	D	G3
2775.047	36024.81	1	D	G2
3261.050	30656.16	10	B	G2, I
4678.160	21369.964	40	B	I
4799.918	20827.885	50	B	I
5085.824	19657.025	8	B	I
6438.472	15527.354	5	B	I
	D. SILVER			
3280.682	30472.72	20	A	I
3383.890	29552.07	50	A	I
4476.048	22334.890	12	B	I
4668.479	21414.276	10	B	I
5209.080	19191.919	12	B	I
5465.497	18291.528	10	A	I
5471.554	18271.279	6	A	I
7687.779	13004.085	20	B	I
8273.519	12083.439	5	B	I
	E. TIN			
2706.505	36937.08	1	D	I
2839.980	35201.19	4	D	I
2863.321	34914.26	3	B	I
3009.146	33222.37	3	D	G2
3175.044	31486.55	5	D	G2
3262.330	30644.13	6	B	I, G2
3800.996	26301.45	1	D	G2
4524.735	22094.567	2	A	I
	F. SODIUM			
4978.585	20080.442	3	D	I
4982.845	20063.275	4	B	I
5682.657	17592.532	6	B	I
5688.224	17575.315	7	B	I
5889.953	16973.371	50	A	I
5895.923	16956.185	35	A	I
6154.229	16244.503	3	B	I
6160.760	16227.282	4	B	I
8183.270	12216.699	3	D	I
8194.811	12199.494	3	D	I
	G. VARIOUS ELEMENTS			
6911.286	14465.104	1	D	I K
6938.975	14407.383	2	D	I "
7664.907	13042.888	5	B	I "
7698.979	12985.167	5	A	I "
6103.642	16379.137	4	D	I Li
6707.844	14903.813	10	D	I Li
7800.227	12816.618	2	D	I Rb
7947.60 −	12578.96	1	D	G1 "
4555.421	21945.737	7	B	I Cs
4593.195	21765.259	4	D	I "
4607.331	21698.482	4	A	I Sr
4572.671	21862.949	5	D	I Be

* These lines have not been measured previously by interference. One of the levels involved in each case appears to be multiple.

triplet $5^3S-6^3P^0$ at wave-length 6928A consists of sharp lines, the triplets $5^3S-7^3P^0$ and $5^3S-8^3P^0$, at 5772A and 5308A are diffuse or multiple in a source of sufficient intensity to register them in a few hours observing time. This lack of sharpness may be associated with an electric effect, since the current was raised to 8 amperes in order to photograph the weakest lines. The wave-lengths reported for these diffuse lines are center of gravity values. The line $5^1S-8^1P^0$ at 5937A proved to be too unstable for measurement at the intensity necessary to register it in a reasonable exposure time. The line $5^1S-6^1P^0$ is also somewhat unstable, yet the wave-length reported for it is probably reproducible to a part in a million, even at high intensities of source.

The use of brass electrodes permitted the measurement of several lines of lead and tin. Copper lines occur in the long wave portion of the spectrum because of the use of copper, brass or sterling silver as one electrode. All the lines of copper measured in this region are published, since they were compared directly with neon, and not used to reduce the plates, as in the shorter region. For the lines common to both, the mean wave-lengths of the copper lines is a part in two million greater than in the table of Burns and Walters.[3] This may be due in part to the greater intensity of source used in the present work.

Silver showed as an impurity in the brass used for electrodes in the shorter region; and those observations made by means of a sterling silver electrode showed the stronger lines of silver in a beautifully sharp condition. The silver lines reported in this paper with probable error "A" may well be considered as standards.

[3] Burns and Walters, *Wave-lengths in the Spectra of the Vacuum Copper Arc*, Publ. Allegheny Obs., Vol. 8, No. 3.

Cadmium was present in nearly every zinc and brass sample. The lines of cadmium which have been well observed previously have somewhat greater wave-length in the present table. The red line is only slightly increased in wave-length by the powerful source, but the effect on the blue lines, which are multiple, was considerably greater.

The beryllium line lacks sharpness; this may be due to electric effect or to the presence of hyperfine structure.

The wave-lengths of the alkalies are center of gravity values excepting in the case of rubidium 7800A. The reported wave-length of this complex line probably refers to one component. The line is very easily self-reversed, it shows a wide hyperfine structure, and no doubt the isotope separation is measurable. The line occurred as a weak impurity because of the previous use of the lamp house in observing rubidium. The most suitable interferometer separations for resolving 7800A were not sought as the line was not on the present program.

Rods of German silver were used as electrodes in making a few exposures; these exposures showed several lines of nickel. The nickel lines agree well with the solar wave-lengths of St. John and others,[1] and there seems to be no need to report these values which for the most part rest on a single observation of each line.

In the column headed "p. e." an A means that an accuracy of a part in two million has been obtained; B indicates a part in a million; C shows that the error may be greater than a part in a million; and D indicates that the value is unreliable. In the short wave region, the prism and grating measurements are by Burns; the interferometer measurements are by Boreman, who also observed the beryllium line. The longer region was observed and measured by Hetzler. We are indebted to the Carnegie Institute of Technology and to Dr. F. M. Walters, Jr., for the use of a Hilger E-1 spectroscope, and for assistance in observing. The short wave grating plates were taken at the U. S. Bureau of Standards, by courtesy of Dr. W. F. Meggers and the late Director G. K. Burgess, Allegheny Observatory, April, 1935.

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Deepest Terms in Ions of the Isoelectronic Sequence A I-Mn VIII

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Radiations corresponding to the energy differences between the terms $3p^6\ {}^1S_0-3p^5\ 4s\ {}^3P_1^0$, ${}^1P_1^0$ in Ti V, V VI, Cr VII, Mn VIII and $3p^6\ {}^1S_0-3p^5\ 5s\ {}^3P_1^0$, ${}^1P_1^0$ in V VI and Cr VII have been observed. These radiations connect the upper states with the deepest terms in each ion and therefore enable the calculation of the ionization potentials. The identification of the lines was facilitated by the use of constant second difference displaced frequency diagrams. The limits of the $3p^6\ {}^1S_0-3p^5$ ms ${}^3P_1^0$, ${}^1P_1^0$ series have been calculated for V VI and Cr VII, and have an estimated error in the value of the deepest terms of 0.5 percent. The values of the deepest terms of V VI and Cr VII, calculated from series limits, make possible the calculation of the absolute value of the deepest terms of Sc IV, Ti V and Mn VIII from a Moseley diagram.

IN a previous report[1] an estimate was given of the absolute value of the ground term $3p^6\ {}^1S_0$ of the argon-like ions Sc IV, Ti V, V VI, Cr VII and Mn VIII. The estimate was based on an almost linear extrapolation of the Moseley diagram for the $3p^5\ 4s\ {}^1P_1^0$ terms of A I, K II and Ca III.[2] It was made by adding the radiation corresponding to the transition ${}^1S_0-{}^1P_1^0$ to the extrapolated value of the ${}^1P_1^0$ term which was obtained from the Moseley diagram. Since then, radiations corresponding to the transitions $3p^6\ {}^1S_0-3p^5\ 5s\ {}^1P_1^0$ and $3p^6\ {}^1S_0-3p^5\ 5s\ {}^3P_1^0$ have been observed in V VI and Cr VII. The discovery of

[1] P. G. Kruger and S. G. Weissberg, Phys. Rev. **46**, 336 (1934).

[2] Data from Bacher and Goudsmit, *Atomic Energy States*.

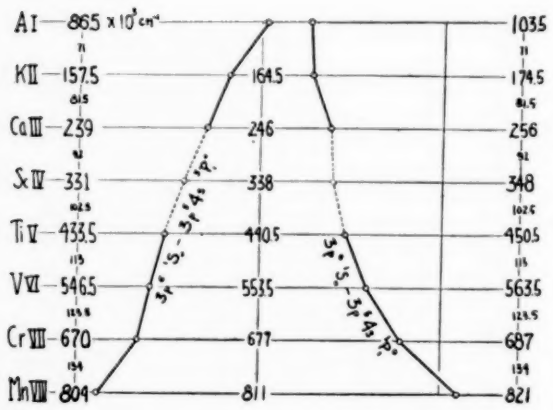

FIG. 1. First series members $3p^6\ {}^1S_0 - 3p^5\ 4s\ {}^3P_1^\circ,\ {}^1P_1$; constant second difference 10,500 cm^{-1}.

the second members of the $^1S_0 - ms\ ^1P_1^0$ and $^1S_0 - ms\ ^3P_1^0$ series enables one to make a calculation of the series limits by use of the Rydberg tables.

All spectrograms were taken with a 21-foot grazing incidence vacuum spectrograph, which has been described previously.[3, 4] The only change in the apparatus was the substitution of three specially constructed General Electric Company 0.3-microfarad pyranol capacitors, in series, for the bank of oil-immersed glass plate capacitors used heretofore. As a result, more intense spectra were obtained for a given exposure time than had been obtained with the glass plate capacitors. The intensity for a given exposure time was also augmented by charging and discharging the capacitors three times a second instead of twice a second. To obtain the first members of the series the necessary exposure times were: Ti, 4 hr., V, 4 hr., Cr, 3 hr., and Mn, 4 hr. The second members in V and in Cr were obtained after 5-hr. exposures. The second members in Mn VIII and possibly the third members in Cr VII appeared after 5-hr. exposures, but the wave-lengths are not reported here because the lines occur in a region in which there are not sufficient standards for accurate measurement. ($\lambda \leqq 86$A for the Mn VIII lines and $\lambda \leqq 94$A for the Cr VII lines.)

When the spectra of Ti, Cr and Mn were photographed, the positive electrode was a cylindrical copper shell in which a piece of pure metal in the form of a hemisphere was mounted. The V electrodes were prepared by heating V_2O_5 powder in a copper shell to red heat in a reducing flame. Since the spectrograms obtained from this electrode showed both V and O lines it was necessary to compare these spectrograms with oxygen spectrograms previously taken in order to obtain a list of lines due to vanadium alone.

[3] P. G. Kruger, Rev. Sci. Inst. **4**, 128 (1933).
[4] P. G. Kruger and W. E. Shoupp, Phys. Rev. **46**, 124 (1934).

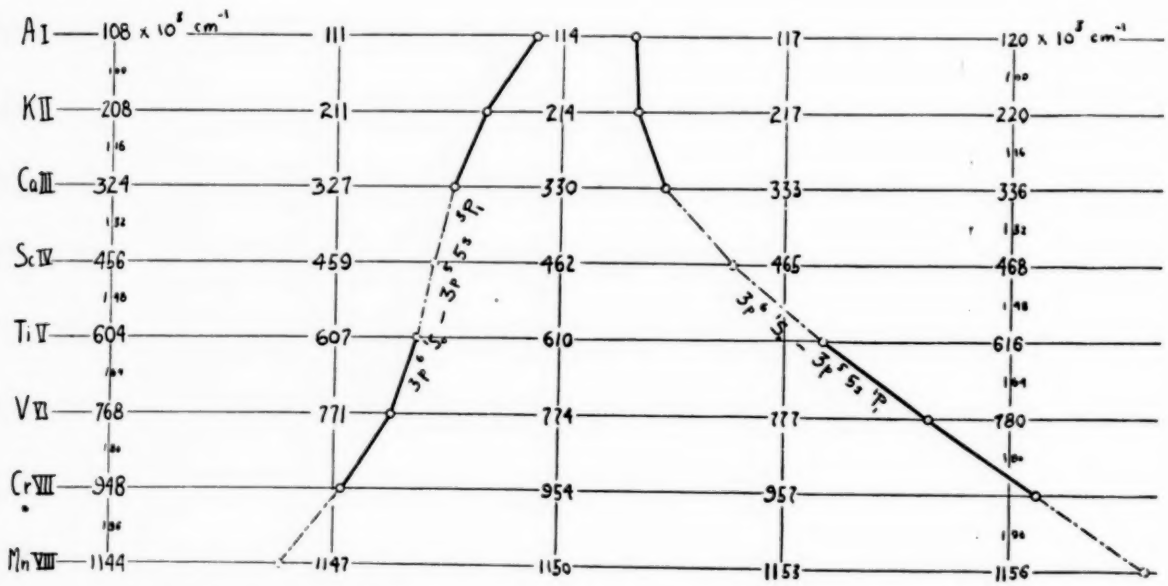

FIG. 2. Second series members $3p^6\ {}^1S_0 - 3p^5\ 5s\ {}^3P_1,\ {}^1P_1$; constant second difference 16,000 cm^{-1}.

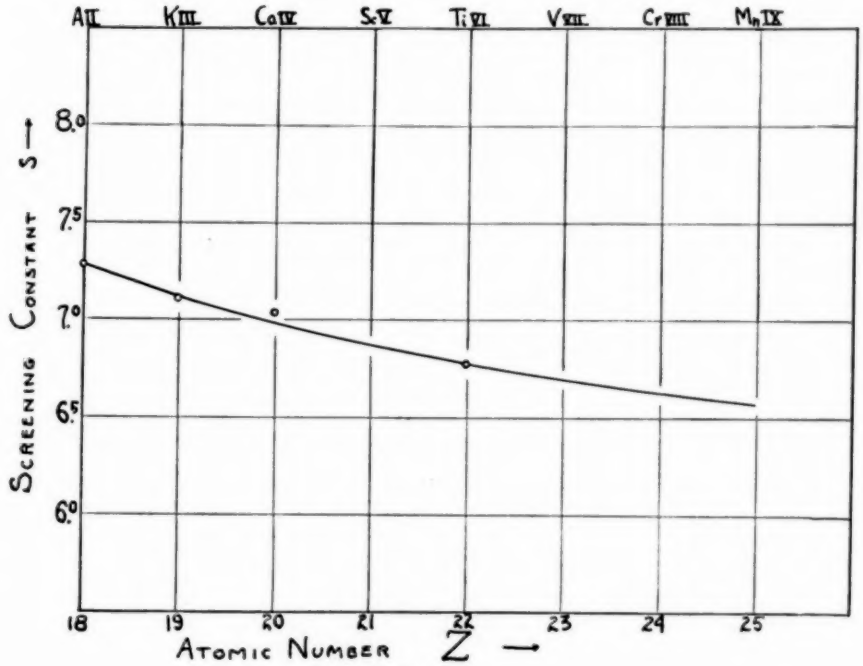

FIG. 3.

A pure copper rod served as the negative electrode in every case.

The method of constant second difference displacement curves,[4] as shown in Figs. 1 and 2 and in Tables VI and VII was used to predict the approximate wave-lengths of the lines sought. The identifications are unambiguous, inasmuch as the lines are relatively isolated and the dispersion very large. In all cases except the second series members in V VI and Cr VII the strongest lines in the region satisfied the condition that the line of longer wave-length (the intercombination line) was the less intense. Moreover, in the course of following the displacement curves through a sequence, the extrapolated values in no case differed by more than 800 frequency units from the observed values. This corresponds to 0.1A at 125A and to 0.3A at 200A. The only case in which several lines occurred sufficiently near each other to raise a question of the identification was in the case of Mn VIII. In this case, the two lines picked were the strongest lines in the region, and the more intense line was of shorter wave-length. In the second members of the series in V VI and Cr VII, the line positions were equally unambiguous, but the line of shorter wave-length was the less intense. This apparently anomalous intensity relationship may be compared with the intensity relationship in the corresponding series of Kr I[5] and Xe I.[6] In these atoms the $^1S_0-{}^3P_1{}^0$ transition is more intense than the $^1S_0-{}^1P_1{}^0$, and the coupling tends toward the *jj* type. It is logical to suppose that the coupling in the argon-like ions tends toward *jj* as the principal quantum number increases since the $^1P_1{}^0$ and $^3P_0{}^0$ terms approach the $^2P_{1/2}$ state of the chlorine-like ions, while the $^3P_1{}^0$ and $^3P_2{}^0$ approach the $^2P_{3/2}$ state of the chlorine-like ions. Thus it may be expected that the second members of the series will have the intensities reversed.

In Table I are listed the wave-lengths, wave

TABLE I. *Observed lines and transitions.*

Ion	Relative intensities	λ(A)	ν(cm⁻¹)	Transitions
Ti V	75	228.898	436876	$3p^6\ {}^1S_0-3p^5\,4s\ {}^3P_1{}^0$
	100	225.337	443780	$3p^6\ {}^1S_0-3p^5\,4s\ {}^1P_1{}^0$
V VI	15	182.050	549300	$3p^6\ {}^1S_0-3p^5\,4s\ {}^3P_1{}^0$
	20	179.323	557653	$3p^6\ {}^1S_0-3p^5\,4s\ {}^1P_1{}^0$
	4	129.574	771759	$3p^6\ {}^1S_0-3p^5\,5s\ {}^3P_1{}^0$
	2	128.382	778925	$3p^6\ {}^1S_0-3p^5\,5s\ {}^1P_1{}^0$
Cr VII	15	148.736	672332	$3p^6\ {}^1S_0-3p^5\,4s\ {}^3P_1{}^0$
	25	146.532	682444	$3p^6\ {}^1S_0-3p^5\,4s\ {}^1P_1{}^0$
	4	105.14	951110	$3p^6\ {}^1S_0-3p^5\,5s\ {}^3P_1{}^0$
	1.5	104.13	960340	$3p^6\ {}^1S_0-3p^5\,5s\ {}^1P_1{}^0$
Mn VIII	10	124.254	804803	$3p^6\ {}^1S_0-3p^5\,4s\ {}^3P_1{}^0$
	15	122.135	818766	$3p^6\ {}^1S_0-3p^5\,4s\ {}^1P_1{}^0$

[5] W. F. Meggers, T. L. de Bruin and C. J. Humphreys, Bur. Standards J. Research **3**, 129 (1929).
[6] W. F. Meggers, T. L. de Bruin and C. J. Humphreys, Bur. Standards J. Research **3**, 731 (1929).

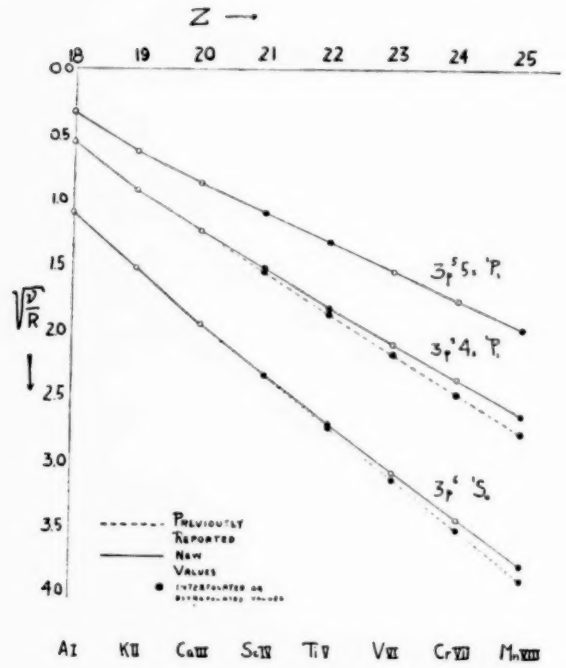

FIG. 4. Moseley diagram.

numbers, and relative intensities of the observed lines, together with the corresponding transitions. For all lines except the two Cr VII lines of shortest wave-length, a linear interpolation between very near Cu secondary standard[7] lines and a correction curve were used to determine the wave-lengths. The Cr VII lines λλ105.14A and 104.13A were calculated by the use of a quadratic formula,[7] using two Be lines λλ100.254A and 88.374A[8] and the Cu line λ109.215A as standards. Since there were no other standards in this region it was impossible

TABLE II. *Correlation of series limits.*

Ion	$L(^1P_1^0)$ (cm^{-1})	$L(^3P_1^0)$ (cm^{-1})	$^1S_0$(ref. 1) (cm^{-1})	$L(^1P_1^0)-L(^3P_1^0)$ (cm^{-1})	$\Delta^3P_{3/2\ 1/2}$ (cm^{-1})
A I	128854	127398	127103.8	1456	1431[a]
K II	258234	256776	256637	1458	2164[a]
Ca III	415568	413267	413127	2301	3056[c]
Sc IV	(602400)[d]	(598800)[d]	602000	(3600)[d]	(4300)[b]
Ti V	(812500)[d]	(807700)[d]	824000	(4800)[d]	5828[c]
V VI	1046420	1040090	1076000	6330	(7600)[b]
Cr VII	1308280	1299700	1359000	8580	(9800)[b]
Mn VIII	(1585000)[d]	(1578000)[d]	1672000	(11000)[d]	(12500)[b]

[a] Data from Bacher and Goudsmit, *Atomic Energy States.*
[b] From screening constants. See Fig. 3.
[c] S. G. Weissberg and P. G. Kruger, Phys. Rev. **47**, 798 (1935).
[d] Estimated from Moseley diagrams similar to Fig. 4.

[7] P. G. Kruger and F. S. Cooper, Phys. Rev. **44**, 826 (1933).
[8] P. G. Kruger and F. S. Cooper, Phys. Rev. **44**, 418 (1933).

TABLE III. *Series limits in rare gas-like ions.*

Ion	$L(^3P_1^0)$ from 2 members (cm^{-1})	$^1S_0$ (cm^{-1})	Percent diff.
Ne I	174312	173930	+0.22
Na II	382795	381528	+0.33
Mg III	648608	646364	+0.34
Al IV	971075	967783	+0.34
Si V	1346639	1342900	+0.27
A I	127397	127103	+0.23
Kr I	113559	112914	+0.57
Rb II	221804	221852	−0.025
Xe I	96335	97835	−1.5

TABLE IV. *Ionization potentials.*

Ion	Ionization potential (volts)	First difference (volts)	Second difference (volts)
A I	15.69		
		15.98	
K II	31.67		3.3
		19.3	
Ca III	51.0		3.7
		23.0	
Sc IV	74.0		2.7
		25.7	
Ti V	99.7		3.0
		28.7	
V VI	128.4		2.7
		32.0	
Cr VII	160.4		2.6
		34.6	
Mn VIII	195.		

TABLE V. *Term values.*

Ion	$3p^6\ ^1S_0$ (cm^{-1})	$3p^5\,4s\ ^3P_1^0$ (cm^{-1})	$3p^5\,4s\ ^1P_1^0$ (cm^{-1})	$3p^5\,5s\ ^3P_1^0$ (cm^{-1})	$3p^5\,5s\ ^1P_1^0$ (cm^{-1})
A I	127103.8	33360.86	31711.62	13468.4	12138.4
K II	256637.	93400.	90176.	43644.	41618.
Ca III	413127.	169200.	165434.	84547.	81729.
Sc IV	(598800)	(268100)	(251200)	(134000)	(129700)
Ti V	(807700)	(370824)	(363920)	(196300)	(189000)
V VI	1040090	490790	482437	268331	261165
Cr VII	1299700	627368	617256	348590	338360
Mn VIII	(1578000)	(771200)	(757200)	(444500)	(428000)

Values in parentheses are estimated from Moseley diagrams of Fig. 4.

TABLE VI. *Radiated frequencies with first and second differences (in cm^{-1}).* First series members.

Ions	$3p^6\ ^1S_0-3p^5\,4s\ ^3P_1^0$			$3p^6\ ^1S_0-3p^5\,4s\ ^1P_1^0$		
A I	93742.9			95392		
		69494			71070	
K II	163237		11196	166462		10161
		80690			81231	
Ca III	243927		(10383)	247693		(11076)
		(91073)			(92307)	
Sc IV	(335000)		(10803)	(340000)		(11473)
		(101876)			(103780)	
Ti V	436876		(10548)	443780		(10093)
		112424			113873	
V VI	549300		10608	557653		10919
		123032			124792	
Cr VII	672332		9439	682445		11529
		132471			136321	
Mn VIII	804803			818766		

TABLE VII. *Radiated frequencies with first and second differences (in cm^{-1}).* Second series members.

Ions	$3p^6\ {}^1S_0 - 3p^5\ 5s\ {}^3P_1^0$			$3p^6\ {}^1S_0 - 3p^5\ 5s\ {}^1P_1^0$		
A I	113655			114965		
		99357.5			100053	
K II	212992.9		16230	215018.8		16326.4
		115587.5			116379	
Ca III	328580.4		(16133)	331398.6		(16521)
		(131720)			(132901)	
Sc IV	(460300)		(16080)	(464300)		(16299)
		(147800)			(149200)	
Ti V	(608100)		(15859)	(613500)		(16225)
		(163659)			(165425)	
V VI	771759		(15692)	778925		(15990)
		179351			181415	
Cr VII	951110		(15839)	960340		(16045)
		(195190)			(197460)	
Mn VIII	(1146300)			(1157800)		

to draw a correction curve, and thus the wavelength may be in error by 0.01A.

In Table II are listed the series limits calculated from two members of the $^1S_0 - \text{ms}\ ^1P_1^0$ series (designated by $L(^1P_1^0)$), and the limits $L(^3P_1^0)$ calculated from two members of the $^1S_0 - \text{ms}\ ^3P_1^0$ series. In the third column are listed, for purposes of comparison, the $^1S_0$ term values previously reported.[1] In the fourth column are the differences $L(^1P_1^0) - L(^3P_1^0)$ and in the fifth column the doublet splitting of the ground state, $^2P_{3/2\ 1/2}$ of the chlorine-like ions A II, K III, etc.

The $^1P_1^0$ and $^3P_0^0$ terms in A I approach the $^2P_{1/2}$ state of A II as a limit, and the $^3P_1^0$ and $^3P_2^0$ terms approach the $^2P_{3/2}$ state of A II. The data in Table II show that this is true for all ions of the A I – Mn VIII isoelectronic sequence. The difference between the limits $L(^1P_1^0)$ and $L(^3P_1^0)$ compares favorably with the known values of the $^2P_{3/2\ 1/2}$ splitting in K III and Ca IV, and with the predicted splitting in V VII and Cr VIII. This prediction is made by assuming the regular trend of the screening constant s with changing Z in the expression for the regular doublet law:

$$\Delta\nu = R\alpha^2(Z-s)^4/n^3l(l+1).$$

A graph of s *vs.* Z is shown in Fig. 3.

The only accurately known deepest term values in the A I – Mn VIII sequence are those of A I and K II, *viz.*, $^1S_0$ of A I is 127,103.8 cm^{-1} and $^1S_0$ of K II is 256,637 cm^{-1}. The $L(^3P_1^0)$ limits are deeper than the correct values in both these cases but in V VI and in Cr VII the $L(^3P_1^0)$ limits are not as deep as the previously[1] reported $^1S_0$ term values. However, the $L(^3P_1^0)$ limits are more nearly correct for the latter cases since they are the result of a limit calculation rather than an extrapolation. The $L(^3P_1^0)$ values for V VI and Cr VII should not be in error by more than ± 0.5 percent. This can be seen from Table III, which gives the results of a calculation of the series limit $L(^3P_1^0)$ from two members of the $^1S_0 - \text{ms}\ ^3P_1^0$ series in the Ne I – Si V sequence and in A I, Kr I, Rb II and Xe I, all of which are rare gas-like, and have similar spectra. Data for the Ne I – Si V sequence are taken from Söderqvist's monograph.[9] The other data are from Bacher and Goudsmit.

In Table IV are listed the ionization potentials of the members of the A I – Mn VIII isoelectronic sequence, and in Table V are listed the values of the deepest terms.

The Moseley diagram from which the interpolations and extrapolations in Tables II and V are made is shown in Fig. 4.

The data used to construct Figs. 1 and 2 are shown in Tables VI and VII.

[9] J. Söderqvist, Nova Acta Reg. Soc. Sci. Upsaliensis, (VI) **9**, No. 7, p. 102 (1934).

Energy Bands in Copper*

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The general method of obtaining energy bands and wave functions for a face-centered lattice has been outlined. The method has been applied to a copper lattice using a corrected Hartree potential field. The energy bands as a function of the internuclear distance have been calculated. The strong overlapping of the *3d* band and the *4s* band is shown. The assignment of electrons to the lowest energy bands leads to a satisfactory explanation of the well-known fact that copper is a good conductor. The various energy bands of the three directions 100, 110 and 111 have been correlated.

WIGNER and Seitz[1] recently introduced the cellular method and applied it to the calculation of the lowest energy state of the conducting electron in a sodium lattice and to the corresponding wave function. Slater[2, 3] extended their ideas to the calculation of higher energy states and wave functions in a body-centered lattice and, in particular, to the higher states of sodium. In this report, the ideas of Wigner, Seitz, and Slater will be extended to a face-centered lattice, in particular to copper.

Wigner and Seitz observed that the potential field acting on an electron in a metal is very approximately spherically symmetric in the neighborhood of a nucleus, so that the Schrödinger equation can be solved by the separation of variables, and numerical integration of the equation for the radial function, as in problems of isolated atoms. They then imagined the crystal to be made up of close-packed cells, one surrounding each nucleus, approximating spheres, but bounded by planes so that they fill all space. If the Schrödinger equation is solved for the electron in one of these cells, subject to certain boundary conditions, then the wave function for the whole lattice can be obtained.

To form the cell for an atom in a face-centered lattice, construct planes which perpendicularly bisect the lines drawn from the nucleus in consideration to its twelve nearest neighbors. The resulting polyhedral cell is a rhombic dodecahedron, as shown in Fig. 1. Each of the twelve faces is a rhombus, and the midpoints of all of the faces are at the same distance from the center.

To solve the Schrödinger equation exactly for the lattice, assuming that the correct potential is given, the procedure would be the following one. The wave equation is solved within the cell, subject to the boundary conditions that the wave function and its normal derivative be continuous in passing across the faces of the cell and satisfy the Bloch[4] condition in passing from one cell to another.

As the exact solution of this problem is impractical at present, it is necessary to proceed by satisfying these conditions approximately. The method actually used will be to solve the Schrödinger equation within the cell, requiring

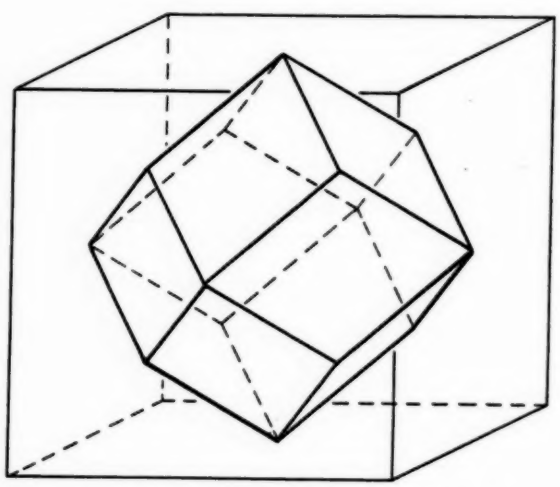

FIG. 1. Polyhedral cell for a face-centered lattice.

* A preliminary report of these results is given in an abstract, Krutter, Phys. Rev. **47**, 810 (1935).

[1] Wigner and Seitz, Phys. Rev. **43**, 804 (1933).

[2] Slater, Phys. Rev. **45**, 794 (1934).

[3] Slater, Rev. Mod. Phys. **6**, 209 (1934).

[4] For discussion, see Sommerfeld and Bethe, "Electronen theorie der Metalle," *Handbuch der Physik*, Vol. 24, second edition.

continuity of the wave function and its normal derivative at the midpoints of the faces of the cell and taking into account the Bloch condition. In a face-centered lattice, this means fitting boundary conditions at twelve points, all at the same distance from the nucleus.

Section 1. Statement of Boundary Conditions

The distance between an atom and a nearest neighbor is also the perpendicular distance between opposite faces of the cell. Accordingly, the boundary condition is that in going from a point on one of the faces of the cell to a perpendicularly opposite point on the opposite face, the wave function is multiplied by $e^{ik\cdot r}$ where $|r|$ represents the perpendicular distance between faces. The normal derivative is multiplied by $-e^{ik\cdot r}$ in the same process.

U, the wave function, can be split up into an even part U_g and an odd part U_u. U_g is unchanged on going from one point to a diametrically opposite point, whereas U_u changes sign in this process. It is convenient to write U in the form $U=U_g+iU_u$. Then if the function is U_g+iU_u at the midpoint of one face, it is U_g-iU_u at the opposite point. Likewise, if the normal derivative is $U_g'+iU_u'$ at the midpoint of one face, then it is $U_g'-iU_u'$ at the other. It should be noticed that in the case of midpoints, perpendicularly opposite and diametrically opposite denote the same thing.

More explicitly the boundary conditions are:

$$U_g+iU_u=e^{ik\cdot r}(U_g-iU_u),$$
$$U_g'+iU_u'=-e^{ik\cdot r}(U_g'-iU_u'),$$

where the U's are computed at the midpoints of the faces. There are six such pairs of conditions for the six pairs of opposite faces. If the terms U_u, U_u', U_g, U_g' are combined, these equations reduce very conveniently to

$$-U_g'/U_u'=U_u/U_g=\tan(k\cdot r/2).$$

Six pairs of equations of this sort give in all twelve equations to be satisfied.

To satisfy these conditions at the midpoints, it is necessary to build up U_g as a sum of six independent functions and similarly six independent functions for U_u. Now this could be done by the use of any number of spherical harmonics, but we select only the twelve lowest spherical harmonics which should reproduce most correctly the energy bands originating from s, p and d levels in the atomic case. The f band will probably not be obtained correctly, since we are not using all of the f functions. The functions which are chosen are: (1) an s function; (2) three p functions with spherical harmonics x/r, y/r, z/r; (3) the five d functions with spherical harmonics xy/r^2, yz/r^2, zx/r^2, $(3z^2-r^2)/r^2$, $(x^2-y^2)/r^2$; and (4) only three of the seven possible f functions, namely, $x(y^2-z^2)/r^3$, $y(x^2-z^2)/r^3$, $z(x^2-y^2)/r^3$.

Let $R=r/2$ be the distance from the nucleus to the midpoint where the boundary conditions are to be satisfied. This distance is the same for all midpoints in a face-centered lattice, i.e., all the faces are at the same distance from the nucleus. We denote the radial part of the wave functions by s, p, d and f. The wave function built up in this manner is $U=U_g+iU_u$, where

$$U_g=As+2[Bxy+Cz(y-x)+Dz(x+y)+E(3z^2-r^2)+F(x^2-y^2)]d/r^2,$$
$$U_u=\sqrt{2}[G(x+y)+H(x-y)+Iz]p/r+2\sqrt{2}[Qz(x^2-y^2)+S\{x(y^2-z^2)+y(x^2-z^2)\}$$
$$+T\{x(y^2-z^2)-y(x^2-z^2)\}]f/r^3,$$

x, y, z are the Cartesian coordinates, and $x^2+y^2+z^2=r^2$.

Boundary conditions are to be satisfied at the midpoints corresponding to values of $\sqrt{2}(x/R)$, $\sqrt{2}(y/R)$, $\sqrt{2}(z/R)$ equal to 110, 1–10, 101, 10–1, 011, 01–1. The corresponding values of $\tan(k\cdot R)$ are denoted by K, L, M, N, O, P where $K=\tan(k_x+k_y)R/\sqrt{2}$, $L=\tan(k_x-k_y)R/\sqrt{2}$, etc.

The twelve equations obtained from the boundary conditions are.

$$K[As+(B-2E)d]-2[Gp+Sf]=0, \quad (1)$$
$$L[As-(B+2E)d]-2[Hp+Tf]=0, \quad (2)$$
$$M[As+(-C+D+E+F)d]-[(G+H+I)p+(Q-S-T)f]=0, \quad (3)$$

$$N[As+(C-D+E+F)d]-[(G+H-I)p-(Q+S+T)f]=0, \quad (4)$$
$$O[As+(C+D+E-F)d]-[(G-H+I)p+(-Q-S+T)f]=0, \quad (5)$$
$$P[As+(-C-D+E-F)d]-[(G-H-I)p+(Q-S+T)f]=0, \quad (6)$$
$$As'+(B-2E)d'+2K[Gp'+Sf']=0, \quad (7)$$
$$As'-(B+2E)d'+2L[Hp'+Tf']=0, \quad (8)$$
$$As'+(-C+D+E+F)d'+M[(G+H+I)p'+(Q-S-T)f']=0, \quad (9)$$
$$As'+(C-D+E+F)d'+N[(G+H-I)p'+(-Q-S-T)f']=0, \quad (10)$$
$$As'+(C+D+E-F)d'+O[(G-H+I)p'+(-Q-S+T)f']=0, \quad (11)$$
$$As'+(-C-D+E-F)d'+P[(G-H-I)p'+(Q-S+T)f']=0. \quad (12)$$

There are twelve simultaneous linear homogeneous equations for the twelve coefficients A, B, $\cdots T$ and, as such, they have nonvanishing solutions only when the determinant of the coefficients is zero. This gives a single relation between the six quantities K, L, M, N, O and P in terms of s, s', p, etc., which are obtained from numerical integration of the Schrödinger equation. Other relations arise because of the fact that they are derived from only three independent quantities, the three components of k (k_x, k_y, k_z). If a definite energy and a definite R are chosen, then the values s, p, d and f at the midpoints are fixed. So, if two variables determining the direction of k are arbitrarily assumed, then for each energy, internuclear distance, and wave normal, these equations will determine the electronic momentum k.

The task is then to look for solutions for which K, L, M, N, O, P are real, or, in other words, for real values of k_x, k_y, k_z. Complex values of k would correspond to damped waves in which we are not interested. The regions of energy and internuclear distance where this condition is satisfied will then correspond to the allowed energy bands. Complex values of k will then correspond to forbidden bands.

Section 2. Solutions of the Equations

If we consider propagation in the xy plane, i.e., $k_z=0$, the equations split up into two sets, one containing four equations and the other containing eight equations. The four equation set contains only the constants C, D, I, Q and the corresponding wave function changes sign on reflection through the xy plane. The set of eight equations contains the remaining eight constants, and its corresponding wave function is unchanged on reflection through the xy plane. These two sets of equations can in principle be solved separately. But, for all twelve coefficients to be different from zero demands that the determinant of each of the two sets of equations be zero. This, however, gives one more condition than before. As a result, the equation must be satisfied by letting the coefficients of one of the two sets be zero and satisfying the determinantal equations connected with the other set.

Set I

Let us consider the first set of equations in which C, D, I, $Q\neq 0$ and all the other coefficients are zero.

$$(-C+D)d'+M[Ip'+Qf']=0,$$
$$(C+D)d'+P[Ip'-Qf']=0,$$
$$M(-C+D)d-(Ip+Qf)=0,$$
$$P(C+D)d-(Ip-Qf)=0.$$

$C+D$ and $D-C$ are chosen as new constants. The determinantal equation then becomes

$$\begin{vmatrix} d' & 0 & Mp' & Mf' \\ 0 & d' & Pp' & -Pf' \\ Md & 0 & -p & -f \\ 0 & Pd & -p & -f \end{vmatrix}=0.$$

Solving this, the relation

$$\left[M^2+\frac{1}{2}\frac{d'}{d}\left(\frac{p}{p'}+\frac{f}{f'}\right)\right]\left[P^2+\frac{1}{2}\frac{d'}{d}\left(\frac{p}{p'}+\frac{f}{f'}\right)\right]=\left[\frac{1}{2}\frac{d'}{d}\left(\frac{p}{p'}-\frac{f}{f'}\right)\right]^2$$

is obtained.

This equation can be solved for any direction in the $k_z=0$ plane, so that the electronic momentum can be obtained as a function of the energy. The mechanics of this type of calculation have been given in detail by Slater[2] and will therefore not be repeated.

In the special directions 100 and 110 these equations break down into even simpler ones.

100 direction, $P=O=0$.

Class I: $C=D$; all other coefficients are zero. We obtain the condition $d'=0$. This is a so-called zero width band. In this particular direction, for the energy for which $d'=0$, the electron can have any value of k. The wave function which fits the boundary conditions is then $U=Dyzd/r^2$.

Class II: $C=-D$; $I, Q, C, D\neq 0$; all other coefficients are zero. The condition

$$K^2=-(2d'pf/dp'f')/(p/p'+f/f')$$

is obtained with the corresponding wave function

$$U=4Dxzd/r^2+i\{\sqrt{2}I(z/r)p+2\sqrt{2}Qz(x^2-y^2)f/r^3\}.$$

110 direction, $M=P$.

Class I: $D=I=0$. The relation $M^2=-d'f/df'$ is obtained with a corresponding wave function

$$U=C(y-x)zd/r^2+i\sqrt{2}Qz(x^2-y^2)f/r^3.$$

Class II: $C=Q=0$. The relation is

$$M^2=-pd'/p'd$$

with the wave function

$$U=2Dz(x+y)d/r^2+i\sqrt{2}I(z/r)p.$$

Set II

Although it is possible to solve set I for any direction in the $k_z=0$ plane, the set of eight equations cannot be solved as easily. However, they can be solved in the particular directions 100 and 110. Since this process is simply algebraic manipulation, only the results will be recorded.

100 direction.

Class III: $B\neq 0$, $G=-H$, $S=-T$; all other coefficients are zero.

$$K^2=-(2pd'f/p'df')/(p/p'+f/f'),$$
$$U=Bxyd/r^2+i\{\sqrt{2}Gyp/r+2\sqrt{2}Sy(x^2-z^2)f/r^3\}.$$

Class IV: $S=T$, $F=E$; all other coefficients are zero.

$$K^2=-d'f/df',$$
$$U=E(z^2-y^2)d/r^2+i\sqrt{2}Sx(y^2-z^2)f/r^3.$$

Class V: $3E=-F$, $G=H$; all other coefficients except A are zero.

$$K^2=-(3s'pd'/Sp'd)/(s'/s+d'/d),$$
$$U=As+2E(y^2+z^2-2x^2)d/r^2+i2\sqrt{2}Gxp/r.$$

110 direction. The 110 direction simplifies considerably, but not so completely as the 100 direction. The eight equation set breaks up into two groups.

Class III: $H, F, T\neq 0$; all other coefficients are zero.

$$M^2=-(2pd'f/p'df')/(p/p'+f/f'),$$
$$U=2F(x^2-y^2)d/r^2+i\{\sqrt{2}H(x-y)p/r+2\sqrt{2}T(y-x)(z^2+xy)f/r^3\}.$$

Classes IV and V will be discussed more completely since they are more complicated. Although we will give only one set of equations, it turns out that there are two cases contained in it. Since $M=P$ in the 110 direction, our original eight equations now become five after splitting off Class III. In this set only A, B, E, G and S are different from zero. The equations reduce to

$$\begin{aligned}
As'+(-B-2E)d'&=0,\\
K[As+(B-2E)d]-2(Gp+Sf)&=0,\\
M[As+Ed]-(Gp-Sf)&=0,\\
As'+(B-2E)d'+2K(Gp'+Sf')&=0,\\
As'+Ed'+M(Gp'-Sf')&=0.
\end{aligned}$$

The determinantal equation of this is

$$\begin{vmatrix}
s' & -d' & -2d' & 0 & 0\\
s' & d' & -2d' & 2Kp' & 2Kf'\\
s' & 0 & d' & Mp' & -Mf'\\
Ks & Kd & -2Kd & -2p & -2f\\
Ms & 0 & Md & -p & f
\end{vmatrix}=0.$$

Solving this, the following equation is obtained:

$$\begin{aligned}
&2K^2M^2p'df'(5sd'+s'd)\\
&+K^2d'(pf'+p'f)(5s'd+sd')\\
&+4KMd'(pf'-p'f)(s'd-sd')\\
&+2M^2d'(pf'+p'f)(2sd'+s'd)+12s'pd'^2f=0.
\end{aligned}$$

This equation is to be solved in conjunction with the relation $K=2M/(1-M^2)$. This is best done graphically as follows: K is plotted as a function of M using the equation $K=2M/(1-M^2)$. The biquadratic equation is then plotted. The intersections of these two curves determine the allowed K and M values, which in turn define k. This is repeated for various energies, which means different coefficients for the biquadratic in K and M since the values of s, s', p, p', etc. depend on the energy.

111 direction

$K=M=O$; $L=N=P=$ zero. It is also possible to treat the original twelve equations for an electron moving in the 111 direction. The equations break down into six groups; the results of the algebraic manipulation are recorded below.

Class I: $C=F$; all other coefficients are zero.

$$d'=\text{zero (zero width band)},$$

while

$$U=C(y-x)(z-x-y)d/r^2.$$

Class II: $B=-2D$, $D=E$, $2G=-I$; all other coefficients except S are zero.

$$K^2=-(4pd'f/p'df')/(3p/p'+f/f'),$$
$$U=2D(3z^2-r^2+z(x+y)-2xy)d/r^2 + i\{\sqrt{2}G(x+y-2z)p/r + 2\sqrt{2}S[x(y^2-z^2)+y(x^2-z^2)]f/r^3\}.$$

Class III: $Q=-2T$, $C=-F$; all other coefficients except H are zero

$$K^2=-(4pd'f/p'df')/(3p/p'+f/f'),$$
$$U=2C(y-x)(x+y+z)d/r^2 + i\{\sqrt{2}H(x-y)p/r + 2\sqrt{2}T(y-x)(z^2+xy+2z(x+y))f/r^3\}.$$

Class IV: $D=-E$, $B=-2D$; all other coefficients are zero. $d'=$ zero, while

$$U=D(r^2-3z^2+z(x+y)-2xy)d/r^2.$$

Class V: $B=D$, $G=I$; all other coefficients except A are zero.

$$K^2=-(2s'pd'/sp'd)/(s'/s+d'/d),$$
$$U=As+2B(xy+xz+yz)d/r^2 + i\sqrt{2}G(x+y+z)p/r.$$

Class VI: $Q=T$; all other coefficients are zero. $f=$ zero.

$$U=iQ\{z(x^2-y^2)+x(y^2-z^2)-y(x^2-z^2)\}f/r^3.$$

Although the twelve equations have been solved for these special cases, it turns out to be simpler, especially for the 100 direction and the 111 direction, to set up our original equations to take into account the symmetry properties of these special directions. Solving with the symmetry property gives very good clues as to how the classes in the various directions are connected to one another.

Section 3. Application to Copper Lattice

Everything, thus far, is applicable to any face-centered lattice. However, to proceed further, it is necessary to confine the discussion to a particular metal. Then given a potential field, it is possible to calculate s, p, d and f, and so be able to determine how the energy varies as a function of k.

In obtaining radial solutions of the Schrödinger equation for a free atom, it is necessary to find solutions which remain finite at infinity. However, in the cellular method, any solution can be used, since only the wave function as far as the cell boundaries is used. The wave function is continued in the next cell in accordance with the Bloch theorem.

Since the correct potential is unknown in the case of copper, it is necessary to take as an approximation a potential field having the correct general characteristics. As a first approximation to the potential field, it seemed advisable to use the Cu^+ field of Hartree.[5] This should be accurate enough to give a general idea of the manner in which the atomic $4s$, $4p$, and higher levels spread into energy bands as the lattice is compressed. In studying the splitting up of the $3d$ level, a slight correction was made. The $4s$ wave function in the field of Cu^+ was calculated, and its contribution to the potential field was determined. The contribution was added to Cu^+ and the contribution of one of the $3d$ electrons, as given by Hartree, was subtracted. This was the potential field used in the calculation of the $3d$ wave functions in the lattice. It is essentially the potential field due to the nucleus and to the $1s^2\cdots 3d^9 4s$ electrons.

Using the potential field discussed, the wave functions were calculated by numerical integration for a set of energy values. In Fig. 2 the energy is plotted as a function of internuclear distance for $s'=0$, $s=0$, $p'=0$, etc. To discuss the energy bands, it is really necessary to plot different sets of energy *versus* internuclear distance curves for different directions of k. The broad features can, however, be discussed by means of this diagram. The $4s$ level at infinite separation spreads into a band, limited by $s'=0$ and $s=0$ as the lattice is compressed. As the

[5] Hartree, Proc. Roy. Soc. **A141**, 282 (1933); **A143**, 506 (1934).

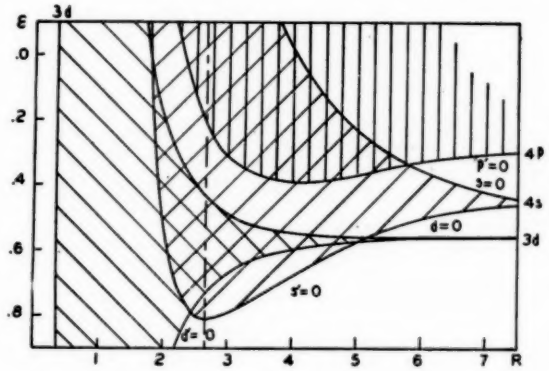

FIG. 2. Energy as a function of internuclear distance. (Energy measured in Rydberg units.)

lattice is compressed still further, the $3d$ band, limited by $d'=0$ and $d=0$, overlaps the $4s$ band, so that at normal separation, denoted by the vertical line in Fig. 2, the $3d$ band and the $4s$ band overlap considerably. Although the normal configuration of the free copper atom is $3d^{10}4s$, as the lattice is compressed the electrons can no longer be described by s or d wave functions, but instead it is necessary to build up the wave function by a combination of s and d wave functions with also a little p and f.

Higher energy bands arising from higher energy atomic levels, overlap in a very complicated fashion. But the approximations used in setting up the problem are not good enough to allow the discussion of the higher bands, even qualitatively. The discussion will therefore be restricted to the lower energy bands.

The minimum of the $4s'=0$ curve is at $r=2.7$. This is in good agreement with the values of the actual effective internuclear distance obtained in the following manner. If the volume occupied by a copper atom in the actual lattice of spacing 3.61 Angstroms is calculated and from it the radius of the sphere having the same volume, then the radius obtained is 2.66 atomic units. The good agreement must mean that the minimum of the total energy curve must be tied up intimately with the minimum of the $4s'=0$ curve. Wigner and Seitz have pointed out the close connection in the case of sodium. The correlation in copper is not as clear.

The unhatched regions at large internuclear distance represent forbidden energy bands independent of the direction of k. These correspond to the well-known energy gaps in atomic levels. As the lattice is compressed to the actual internuclear distance, the energy gaps depend on the direction of k and are consequently not represented in this diagram.

More information can be obtained if the dependence of k on the energy is discussed. To do this, it is convenient to discuss a momentum space, in which certain zones are formed. If the energy contours are plotted in this space, the gaps in energy come at the boundary of the zones. For a detailed discussion of this, the reader is referred to Slater.[3] It is more convenient in the case of copper to cut through this zone along three particular lines. These are the 100, 110 and 111 directions. Quantitative calculations can be carried out only in the 100, 110 and 111 directions. But these are sufficient to give a general idea of all directions. The first problem that arises is that of accounting for the eleven electrons of the $3d^{10}4s$ normal configuration, when the lattice is compressed. This can be done if the energy *versus* k curves are studied. In Fig. 3, the energy is plotted as a function of k at $R=2.6$ for propagation in the 100 direction. Class V, for this direction, splits into two parts, so that for the range of energy shown, there are six different energy *versus* k curves. The vertical line denotes the boundary of the first momentum

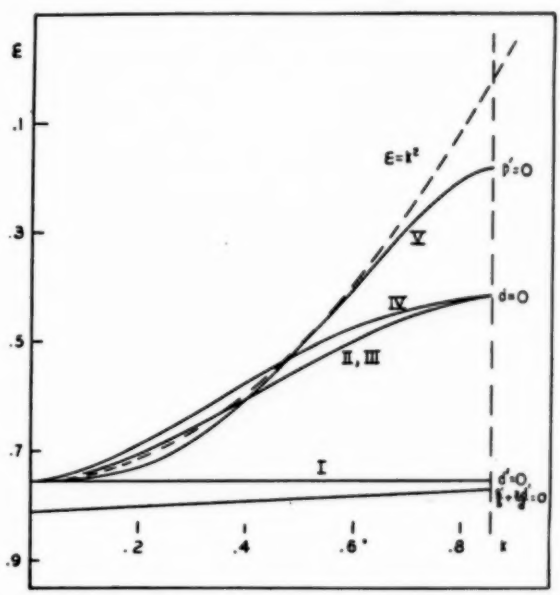

FIG. 3. Energy as a function of momentum for an electron moving in 100 direction. ($R=2.6$.)

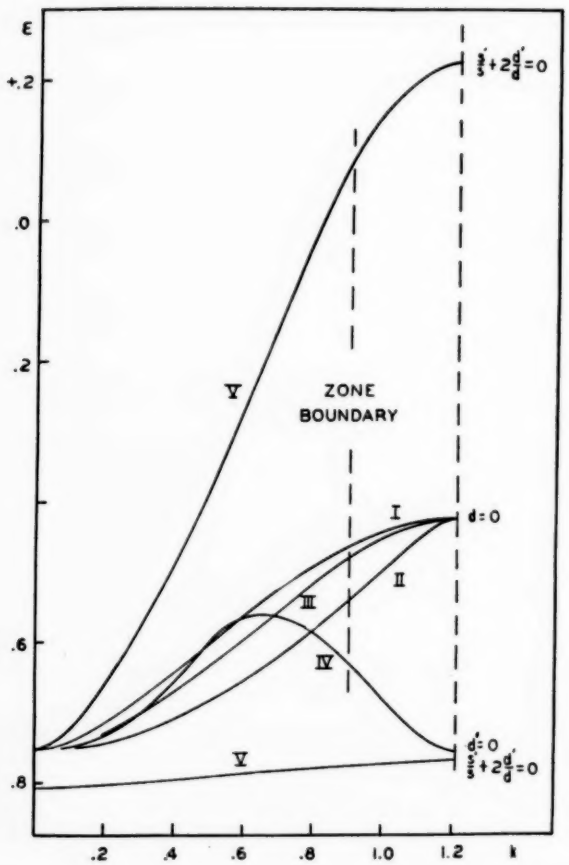

FIG. 4. Energy as a function of momentum for an electron moving in 110 direction. ($R=2.6$.)

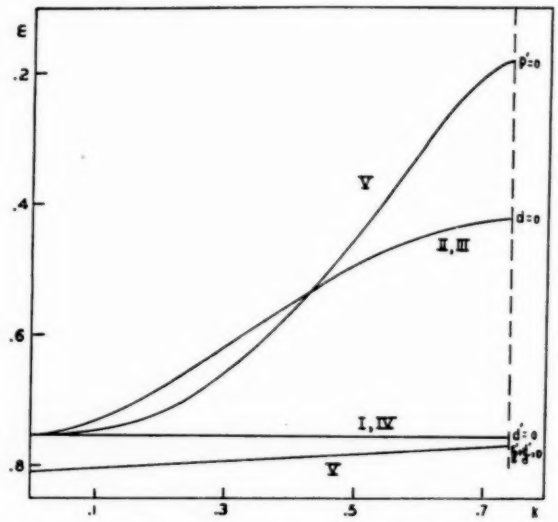

FIG. 5. Energy as a function of momentum for an electron moving in 111 direction. ($R=2.6$.)

zone. The diagram is repeated continuously as the value of k is increased. For higher energies there will be other bands, but these cannot be calculated accurately with the method used thus far.

Now the electrons will fill the bands, first filling the lower ones. Two electrons (degeneracy in spin) are assigned to each band. This leaves the Class V top band only half filled, so that there are 10 electrons filling 5 bands completely. The eleventh electron is in an unfilled band. This electron will play an important part in discussions on conductivity. Electrons in unfilled bands are the conduction electrons. Nonconductors have all filled bands.

In Figs. 4 and 5, the energy as a function of k at $R=2.6$ is plotted for propagation in the 110 and 111 directions. The vertical lines denoting the edge of the zone come at different values of k in each different direction. The assignment of electrons again leaves the bands denoted by Class V only half filled. And again, the Class V band is split in two. This indicates that the bands denoted by Class V in the three directions 100, 110 and 111 are slices of the same band.

The next point of interest is the correspondence between the energy *versus* k curve of the conducting electron and the free electron parabola $\epsilon=k^2$ in atomic units. In the 100 direction (see Fig. 3) the correspondence is very good. In Fig. 6, the top Class V bands are plotted on the same scale for the different directions. It is seen that the slope of the various energy *versus* k curves agree closely with the slope of the free electron

TABLE I.

CLASS	100	110	111
I	$d'=0$	$M^2=-d'f/df'$	$d'=0$
II	$K^2=-2pd'f/d(pf'+fp')$	$M^2=-pd'/p'd$	$K^2=-4pd'f/d(3pf'+fp')$
III	$K^2=-2pd'f/d(pf'+fp')$	$M^2=-pd'f/d(pf'+fp')$	$K^2=-4pd'f/d(3pf'+fp')$
IV	$K^2=-d'f/df'$	See Graph	$d'=0$
V	$K^2=-3s'pd'/p'(ds'+2d's)$	See Graph	$K^2=-2s'pd'/p'(s'd+sd')$

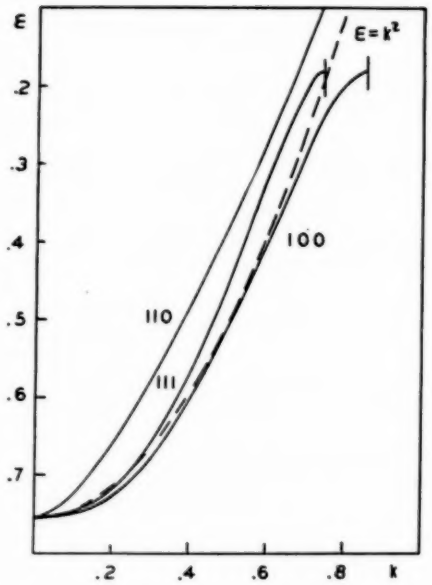

FIG. 6. Comparison of energy *versus* momentum curves for Class V. ($R=2.6$.)

curve for values of k corresponding to a half filled first momentum zone.

In Fig. 7, the energy contours for the conduction electron have been plotted in the $k_z=0$ section of the first zone. If the electron were exactly free electron-like, the contours would be exactly circles. For small values of k, the curves are decidedly not free electron curves. However, for larger values of k, the contours approximate circles.

The real part of the wave function for an electron moving in the 100 direction as seen by cutting through in the 110 direction was plotted for $k=0.596$ with $R=2.6$ for the distance between atoms. The correspondence between this curve and the real part of the $e^{ik\cdot R}$ of a free electron, i.e., $\cos(k\cdot r)$, was found to be satisfactory. This concludes the various checks of the free electron behavior of the conduction electron.

It should also be mentioned that if a wave function is computed in any direction except those directions along which boundary conditions are satisfied, the wave functions will not fit exactly as we pass from cell to cell in ordinary space.

The final remaining point of interest is that of the correlation of the various classes for the

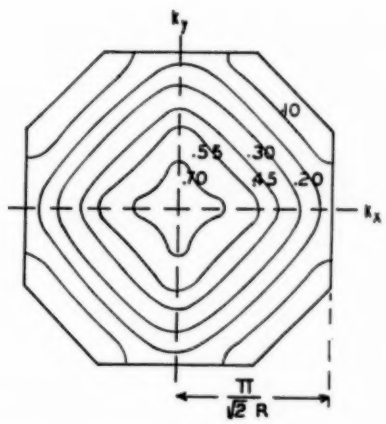

FIG. 7. Energy contours of Class V, $k_z=0$ and $R=2.6$. in the first zone of momentum space.

three directions. This is necessary, as it is desirable at least to be able to take average values for example of dE/dk for various directions for a given energy. The various bands, although solved for different directions, have been correlated by consideration of the nodal properties of the wave functions of the various classes. This correlation is given in Table I.*

The general method of obtaining energy bands and wave functions for a face-centered lattice has been outlined. The method has been applied to a copper lattice using a corrected Hartree potential field. The energy bands as a function of the internuclear distance have been calculated. The strong overlapping of the $3d$ band and the $4s$ band is shown. The assignment of electrons to the various energy bands leads to the result that, theoretically, copper is a good conductor, a well-known experimental fact. The various energy bands of the three particular directions 100, 110, 111 have been correlated. For more quantitative results than those obtained, the approximations used in this report must be improved. The first and most important step in this direction is the task of obtaining a better potential field. This would take the form of a self-consistent Hartree problem for metals.

The author wishes to express his appreciation to Professor J. C. Slater and Dr. G. E. Kimball for many helpful discussions.

*_Note added in proof:_ It appears from further study that these correlations must be revised. See a forthcoming paper by J. C. Slater.

Diamagnetism of Alkyl Acetates†

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Susceptibility measurements on the first five primary alkyl acetates and on methanol, made with the manometric balance of Wills and Boeker over the range 5°–70°, are described. The results show a very slight variation of susceptibility with temperature and an indication of increasing temperature dependence for higher members of the acetate series. The molecular susceptibility of CH_2 is found to be additive in agreement with Pascal's law. The magnetic properties of $NiCl_2$ solutions are discussed with special regard to the work of Fahlenbrach, and experiments on $NiCl_2$ solutions as used for calibrating the manometric balance are described. No variation in the calibration depending on the method of preparing the solutions was found.

DIAMAGNETISM OF ALKYL ACETATES

IN the study of the influence of temperature on the susceptibility of organic compounds it is of interest to determine the effect of a regular change in constitution of the molecule such as occurs, for instance, in the chain compounds. The results of Cabrera and Fahlenbrach[1] on the primary alcohols have shown the value of investigating a series as a whole as compared with measurements on a single substance chosen as typical of a group.

In the present investigation susceptibility determinations over a range of temperatures were made on the first five of the primary alkyl acetates, *viz.* methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl, and on methanol. In continuing the work on susceptibilities inaugurated by Wills and Boeker[2] the alkyl acetates were chosen with a view to supplementing the magnetic data obtained (at room temperature) for the same series by Boorse[3] in his measurements of magnetic birefringence. These acetates may be regarded as formed by the successive addition of a CH_2 group to an acetic acid molecule and experiments upon them may be expected to furnish a test of the diamagnetic additivity of the CH_2 group.

Preliminary to the measurements on the organic liquids just mentioned a study was made of the magnetic properties of nickel chloride solutions used in calibrating the magnetic balance employed in the present investigation in order to make sure that there could be no error in the calibration resulting from a possible variation on the magnetic moment of nickel such as has been recently reported by Fahlenbrach,[4] whose experiments indicated that the susceptibility of nickel chloride in solution might depend upon the concentration and method of preparing the solutions.

APPARATUS AND METHOD

The apparatus used was the manometric balance of Wills and Boeker.[2] This is a device for balancing the force exerted by a magnetic field upon a standard liquid by a corresponding force exerted by a second magnetic field upon a liquid whose susceptibility is to be measured. Several modifications, to be mentioned presently, were made, however, resulting in greater facility of operation and economy in the amount of material used. A schematic diagram is shown in Fig. 1 from which certain details have been omitted for the sake of simplicity. P_0 and P indicate the rear faces of two twin pairs of pole pieces which are cemented to the two core faces of an electromagnet. The balance itself is made of Pyrex glass throughout and consists of two branches, one of which is filled with the standard liquid and the other with the liquid whose susceptibility is to be measured. The two liquids are separated by mercury (indicated by the shaded areas of the diagram). Filling can be accomplished by means of the thistle tubes at the top, or, after a preliminary filling, by drawing

† A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

[1] B. Cabrera and H. Fahlenbrach, Zeits. f. Physik **85**, 568 (1933).

[2] A. P. Wills and G. F. Boeker, Phys. Rev. **42**, 687 (1932).

[3] H. A. Boorse, Phys. Rev. **46**, 187 (1934).

[4] H. Fahlenbrach, Ann. d. Physik **13**, 265 (1932); **14**, 521 (1933).

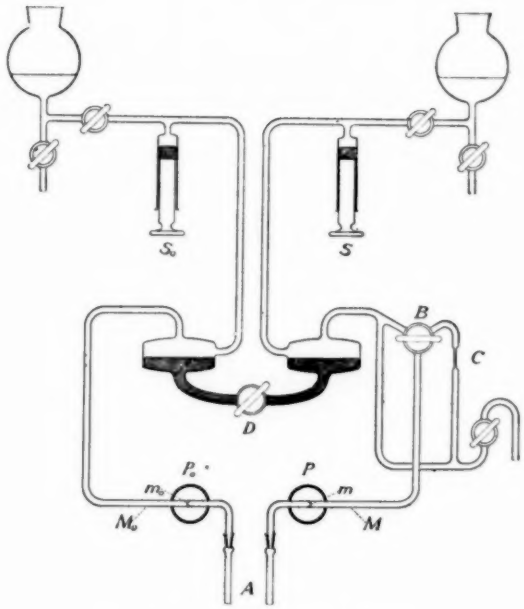

FIG. 1. The manometric balance.

liquid up through the auxiliary tubes A[5] which connect with the apparatus by means of ground glass joints. When the apparatus has been filled the liquid in each branch is drawn back by means of two glass syringes S_0,S so that the two menisci are in the horizontal portions of the meniscus tubes M_0,M between the two pairs of pole pieces corresponding to P_0 and P, as indicated by m_0 and m. These syringes, which replace the heating coils used by Wills and Boeker to adjust the menisci, are operated by fine-thread screws;* their plungers are lubricated with glycerine and are separated from the liquid in the tubes by mercury. The positions of the menisci are determined by cross-hair settings in two telescopes* equipped with micrometer eyepieces. With the stopcock D open and the three-way stopcock B[6] turned to connect the meniscus tube M with the capillary tube C, the left meniscus is kept at a predetermined fixed position, while that of the right is varied until balance is obtained. Balance is indicated by the lack of motion of suspended particles in C as observed by a microscope* when the field is thrown on and off. If both branches are filled with the same liquid at the same temperature the balance position gives the zero setting, i.e., the setting for which the fields acting on the two menisci are equal. If now the temperature of the liquid within M_0 is changed (temperature is regulated by means of water jackets* surrounding M_0 and M) or if the liquid within M_0 is replaced by a different liquid, the right meniscus m must be moved into a region of different field strength in order to restore balance. The difference between this new setting and the zero, as determined by the micrometer eyepiece of the telescope, corresponds to a change in susceptibility on the right which can be computed when the apparatus has been calibrated.

If the two meniscus tubes M_0 and M contain liquids whose volume susceptibilities are κ and κ_0, respectively, and whose free surfaces are in contact with a medium of susceptibility κ_a (air or helium), then the condition for balance under the influence of the magnetic fields when the field strengths at the menisci are H_0 and H, respectively, is:

$$\tfrac{1}{2}(\kappa-\kappa_a)H_0^2=\tfrac{1}{2}(\kappa_0-\kappa_a)H^2,$$

which may be written

$$\kappa/\kappa_0=H^2/H_0^2+(\kappa_a/\kappa_0)(1-H^2/H_0^2), \qquad (1)$$

or, to a sufficient degree of approximation,

$$\frac{H^2}{H_0^2}=\frac{\kappa}{\kappa_0}+\frac{\kappa_a}{\kappa_0}\left(\frac{\kappa}{\kappa_0}-1\right)+\left(\frac{\kappa_a}{\kappa_0}\right)^2\left(\frac{\kappa}{\kappa_0}-1\right). \qquad (2)$$

In measuring temperature variations of susceptibility the liquid is usually the same in both tubes and is maintained in contact with helium by means of a helium bulb* which can be connected with the meniscus tube outlets. One meniscus tube is kept at 20°C while the temper-

[5] In the original apparatus the only provision for filling was the thistle tubes at the top and this required the use of a large amount of liquid for flushing. The present arrangement makes it necessary to flush only a relatively small portion of tubing.

* Not shown.

[6] The stopcock B controls a by-pass arrangement which was introduced to permit drawing in fresh liquid whenever desired without disturbing the particles in C. The frequent occurrence of sticking at the menisci when water or aqueous solutions are under test and the untrustworthiness of such readings when even a small trace of sticking is present make necessary frequent cleaning of the tubes with chromic acid cleaning solution and the by-pass proved an important time saver in both cleaning and filling.

* Not shown.

ature of the other is varied. Noting that when helium is used κ_a/κ_0 is negligible, we have from (1) for the case where M is at 20°:

$$\frac{\kappa}{\kappa_{20}}=\frac{H^2}{H_0^2} \quad \text{or} \quad \frac{\chi}{\chi_{20}}=\frac{\rho_{20}}{\rho}\frac{H^2}{H_0^2}, \tag{3}$$

where ρ represents the density and χ the mass susceptibility κ/ρ.

The method of calibrating the field, i.e., the determination of the ratio H^2/H_0^2 for different settings of the variable meniscus, as described in previous papers, has been modified in the present work as follows. The calibrating solutions of nickel chloride were prepared from a mother solution of nickel chloride that had been made neutral against air—not, as in the previous work, against helium—at 20.7°C. A calibrating solution, prepared by adding to m grams of this neutral solution μ grams of water, has a mass susceptibility χ_n determined by the following relation (Wiedemann's law):

$$(\mu+m)\chi_n=m\chi_s+\mu\chi_0,$$

where χ_s is the mass susceptibility of the neutral solution and χ_0 the susceptibility of water. If we let ρ_s represent the density of the neutral solution and put $m/\mu=\delta$, we have:

$$\frac{\chi_n}{\chi_0}=\frac{1}{1+\delta}\left(1+\delta\frac{\rho_0}{\rho_s}\frac{\kappa_a}{\kappa_0}\right), \tag{4}$$

since the volume susceptibility of a solution neutral against air must equal the volume susceptibility of air. In terms of volume susceptibilities (4) becomes:

$$\frac{\kappa_n}{\kappa_0}=\frac{\rho_n}{\rho_0}\frac{1}{1+\delta}\left(1+\delta\frac{\rho_0}{\rho_s}\frac{\kappa_a}{\kappa_0}\right). \tag{5}$$

In calibrating the apparatus the right branch is filled with water and the left with a nickel chloride calibrating solution. Then the two menisci, which are left in contact with air, are adjusted as described above until balance is obtained. To determine the ratio H^2/H_0^2 for the two meniscus positions at balance, corresponding to a scale reading s, say, for the right-hand meniscus, the expression for κ_n/κ_0 from (5) is substituted for κ/κ_0 in (2), from which we obtain upon reduction the relation:

$$\frac{H^2}{H_0^2}=\frac{\rho_n}{\rho_0}\frac{1}{1+\delta}=\frac{1}{1+\delta\rho_0/\rho_s}, \tag{6}$$

neglecting terms smaller than 10^{-5} since variations in H^2/H_0^2 smaller than this cannot be detected. In this way, by using a series of calibrating solutions, the ratio H^2/H_0^2 as a function of s can be determined and a calibration curve constructed. (Cf. Fig. 2.) The field was calibrated over a range sufficient to accommodate a 7.3 percent change in volume susceptibility corresponding to an actual displacement of m from its zero position of about 2.5 mm or about 1/6 the diameter of the pole face P. Eq. (6) presupposes, of course, that the calibration is carried out at the temperature of neutrality. The expression on the right is obtained by assuming that the volume of a calibrating solution is simply the sum of the volumes of the neutral solution and water that were mixed in its preparation. Since a neutral solution contains approximately 2 percent nickel chloride, any error in assuming additivity of volumes is negligible.

The advantage of this method becomes apparent when it is noted that Eq. (6) is exactly the equation that applies if the field is calibrated with the liquids in contact with helium instead of air and the calibrating solutions are prepared from a mother solution neutral against helium.[7] That is, this method enables one to calibrate with open meniscus tubes without correcting for the susceptibility of air.

The susceptibilities of the organic liquids are determined relative to water by balancing the liquid whose susceptibility is to be measured against a comparison solution of nickel chloride[8] prepared in the same way as the calibrating solutions, except that this comparison solution must be made from a solution neutral against helium. The susceptibility κ_n of such a comparison solution is given by the equation:

$$\kappa_n=\frac{\rho_n}{\rho_0}\frac{\kappa_0}{1+\delta} \tag{7}$$

and, if κ_L be the susceptibility of the liquid, we

[7] Cf. Wills and Boeker, reference 2.

[8] The diamagnetism of organic liquids is generally too small to permit balancing directly against water in the manometric balance.

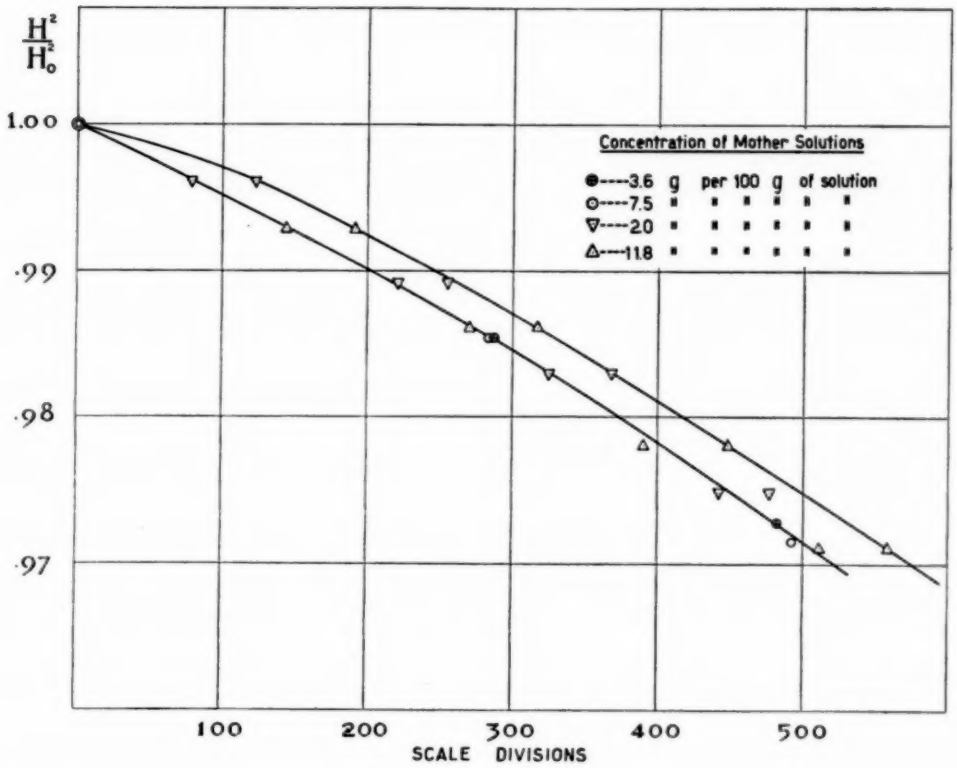

FIG. 2.

have by substituting κ_L/κ_n for κ/κ_0 in (1), using the value of κ_n from (7):

$$\frac{\chi_L}{\chi_0}=\frac{\rho_0}{\rho_L}\frac{\kappa_L}{\kappa_0}=\frac{\rho_n}{\rho_L}\frac{1}{1+\delta\left[\frac{H^2}{H_0^2}+\frac{\kappa_a}{\kappa_0}\left(1-\frac{H^2}{H_0^2}\right)\right]}.$$

The absolute susceptibilities are then computed by taking for the susceptibility of water $\chi_0=0.72\times10^{-6}$.

NICKEL CHLORIDE AS A MAGNETIC STANDARD

The methods for calibrating and for determining the absolute susceptibilities assume that the susceptibility of aqueous solutions prepared by diluting neutral nickel chloride solutions may be computed by Wiedemann's law. This is equivalent to assuming that the magnetic moment of nickel in the calibrating solutions is independent of concentration, since departures from the rule of additivity embodied in Wiedemann's law are generally regarded as indicative of a change in magnetic state. In support of this assumption may be cited the work of Bruins,[9] Brant,[10] Foëx,[11] Cabrera and Dupérier,[12] all of whom found the susceptibility of nickel in solution independent of concentration and put the magnetic moment of Ni^{++} at 16 Weiss magnetons. All but Brant, who worked at room temperature only, investigated the dependence on temperature and found that nickel in solution obeyed Curie's law. However, more recently Foëx and Kessler[13] and Fahlenbrach[14] have reported experiments indicating that the magnetic moment of nickel was not constant. The former found a variety of nickel that obeyed Weiss' law and had a moment of 17 W.m. This moment was nevertheless independent of concentration and after the solution had been heated over 100°C the nickel was found to have the usual moment 16. Fahlenbrach's results, on

[9] Bruins, Akad. Amsterdam **18**, 246 (1915) (cited by Foëx, see note 15).
[10] L. Brant, Phys. Rev. **17**, 697 (1921).
[11] G. Foëx, Ann. d. Physik (9) **16**, 224 (1921).
[12] B. Cabrera and A. Dupérier, J. de physique **6**, 121 (1925); nickel nitrate was used.
[13] G. Foëx and B. Kessler, Comptes rendus **192**, 1638 (1931).
[14] H. Fahlenbrach, reference 4.

the other hand, seemed to show that the magnetic moment of the nickel ion as calculated from the susceptibility of aqueous nickel chloride solutions depended in some cases both on the concentration and on the method of preparing the solutions. Fahlenbrach made up mother solutions of nickel chloride having concentrations of 7.310, 4.217, 9.32, 4.16, 8.29 g per 100 cc of solution, all showing approximately the same moment for nickel, and found for dilutions of the first two more concentrated solutions a magnetic moment independent of concentration and identical with the moment of the mother solutions (15.5). But dilutions of the weaker mother solutions showed increasing moment with increasing dilution. Finally, in the case of an immediate dilution (i.e., a dilution made immediately after preparation) of the 8.29 solution he found a larger moment than for an equal dilution of the same mother solution made several days later. In all cases the nickel obeyed Weiss' law.[15]

In Fahlenbrach's paper the results are presented graphically to show the reciprocal of the Ni^{++} susceptibility as a function of the absolute temperature, the points that determine the curves having been computed from the observational data. The absence of numerical data on the susceptibilities of the nickel chloride solutions themselves makes difficult any estimate of the bearing of his findings on our use of nickel chloride as a standard. Obviously, however, if the same sort of variation in the susceptibility of nickel occurs in our calibrating solutions our method of measuring susceptibilities is quite unreliable. Hence, although our ability to reproduce results after many months, using different sets of calibrating solutions differently prepared, provides considerable indirect evidence for the reliability of our method, it was deemed important to determine whether variations in the method of preparing the calibrating solutions had any influence on the calibration. For this purpose four mother solutions were prepared, two having concentrations such that their dilutions should, in the light of Fahlenbrach's results, show no dependence of susceptibility on concentration, and two whose dilutions should show such dependence. From these were prepared four neutral solutions (the weakest mother solution was made up to be as near neutral at room temperature as possible) and these neutral solutions were then used to prepare calibrating solutions having concentrations ranging from 0.008 to 0.06 g $NiCl_2$ per 100 g of solution. With these the apparatus was then calibrated in the regular manner. Fig. 2 shows two calibration curves made on different occasions for somewhat different parts of the field, but with the same solutions. All calibration points corresponding to the same mother solutions are marked with the same index. These mother solutions had concentrations of 3.6, 7.5, 11.8, 2.0 and the corresponding indices are shown in the legend. Although these points show more scattering than the later calibrations that were used for the acetate measurements, there is no evidence that the calibration is dependent upon the original concentrations of the mother solutions. For the range of concentrations here used the general indication is that the susceptibilities of the calibrating solutions, as computed by Wiedemann's law, depend only on the neutral solutions so that any set of calibrating solutions gives the same result independent of the concentrations of the mother solutions. These results are not, of course, a contradiction of Fahlenbrach's findings since they serve only to establish the uniqueness of the calibration curves.

Preparation of Chemicals

Samples of the five acetates were obtained from the Eastman Kodak Company. In addition, a sample of ethyl acetate (reagent grade) was secured from Merck. All were carefully distilled and only the best fraction of each was used for the determination of the absolute susceptibilities. The boiling points are shown in Table II. The measurements of temperature variation of susceptibility include runs made with other fractions of the distillate as well. The methanol was triple

[15] Foëx, J. de phys. et rad. (7) **3**, 337 (1932); (7) **4**, 517 (1933), has regarded these results as evidence of a new magnetic state of nickel and suggests their explanation on the basis of a principle of uniformization according to which in any given sample the paramagnetic ion can exist in only one state, which state might be assumed to prevail during any change of state in the sample (solution, dilution) provided the change were slow enough. While the agreement of Fahlenbrach's curves with Weiss' law supports this principle, Fahlenbrach's emphasis on uniformity of procedure in preparing solutions makes doubtful the applicability of Foëx's suggestion as an explanation for the dependence on concentration.

distilled from the synthetic product of the Chemical Solvents Company, the last distillation being over magnesium.

Susceptibility-Temperature Measurements

The results of the measurements of relative temperature variation are summarized in Table I; in Figs. 3 and 4 the experimental curves showing volume susceptibility as a function of temperature for propyl and amyl acetates are reproduced. The experimental curves for all six liquids show much the same characteristics and these two may be taken as typical. The values κ/κ_{20} for the volume susceptibilities relative to 20° given in the table have been found by interpolation with the aid of the experimental curve for each substance and from these values the relative mass susceptibilities χ/χ_{20} have been computed. In addition, the table gives for each liquid the average and greatest deviations, Δ_{ave} and Δ_m, of the experimental points from the κ/κ_{20} curve. Experimental points have been indicated only for κ/κ_{20} in Figs. 3 and 4 since the χ/χ_{20} curves are simply the plot of the values given in the tables.

The experiments on methanol were made as a preliminary investigation of the difficulties that might be encountered with hygroscopic liquids. Methanol was chosen for this purpose because of its low cost compared with the acetates and to provide a comparison with the work of other experimenters. It was found necessary not only to dry the helium before admitting it to the apparatus but to put a layer of calcium chloride on the floor of the helium bulb before reproducible measurements could be made on methanol.

A similar difficulty was found in the case of methyl and ethyl acetates, but the use of calcium chloride failed to overcome it. Ultimately, by taking a zero reading at 20° after each determination at a higher (or lower) temperature and correcting for slight zero shifts it was possible to obtain reproducible results for methyl acetate up to about 45° and for ethyl acetate to about 50°. When these temperatures were exceeded zero shifts too large to be corrected occurred and the attempt to go higher had to be abandoned. Just what the changes were that took place at these temperatures is not fully understood.

With the remaining three acetates there was practically no difficulty of this sort and it was possible to carry them up over 70°, beyond which temperature the behavior of the apparatus becomes too unstable and constant temperature too difficult to maintain for precise measurement.

Methanol and the first three acetates show very nearly the same slight decrease in dia-

Table I.

Methanol				Ethyl acetate				n-Butyl acetate			
T	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	T	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	T	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}
10	1.0124	1.0119	1.0005	5	1.0201	1.0210	1.0009	6	1.0162	1.0164	1.0002
20	1.0000	1.0000	1.0000	10	1.0135	1.0140	1.0005	10	1.0116	1.0117	1.0001
30	0.9876	0.9880	0.9996	20	1.0000	1.0000	1.0000	20	1.0000	1.0000	1.0000
40	0.9752	0.9760	0.9992	30	0.9864	0.9860	0.9996	30	0.9883	0.9882	0.9999
50	0.9628	0.9638	0.9990	40	0.9727	0.9719	0.9992	40	0.9765	0.9769	1.0004
				50	0.9591	0.9580	0.9989	50	0.9647	0.9656	1.0009
$\Delta_m(\kappa/\kappa_{20})=0.0010$		$\Delta_{ave}(\kappa/\kappa_{20})=0.0004$		$\Delta_m(\kappa/\kappa_{20})=0.0010$		$\Delta_{ave}(\kappa/\kappa_{20})=0.0004$		60	0.9527	0.9535	1.0008
								70	0.9407	0.9408	1.0001
								$\Delta_m(\kappa/\kappa_{20})=0.0005$		$\Delta_{ave}(\kappa/\kappa_{20})=0.0002$	

Methyl acetate				n-Propyl acetate				n-Amyl acetate			
T	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	T	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	T	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}
5	1.0206	1.0216	1.0010	10	1.0125	1.0130	1.0005	10	1.0109	1.0117	1.0008
10	1.0138	1.0144	1.0006	20	1.0000	1.0000	1.0000	20	1.0000	1.0000	1.0000
20	1.0000	1.0000	1.0000	30	0.9874	0.9871	0.9997	30	0.9890	0.9885	0.9995
30	0.9861	0.9856	0.9995	40	0.9747	0.9740	0.9993	40	0.9779	0.9786	1.0007
40	0.9861	0.9856	0.9991	50	0.9619*	0.9610	0.9991	50	0.9668	0.9682	1.0015
				60	0.9493*	0.9481	0.9988	60	0.9555	0.9570	1.0016
$\Delta_m(\kappa/\kappa_{20})=0.0010$		$\Delta_{ave}(\kappa/\kappa_{20})=0.0004$		70	0.9361*	0.9350	0.9989	70	0.9441	0.9445	1.0004
				$\Delta_m(\kappa/\kappa_{20})=0.0004$		$\Delta_{ave}(\kappa/\kappa_{20})=0.0002$		$\Delta_m(\kappa/\kappa_{20})=0.0010$		$\Delta_{ave}(\kappa/\kappa_{20})=0.0003$	

* Extrapolated.

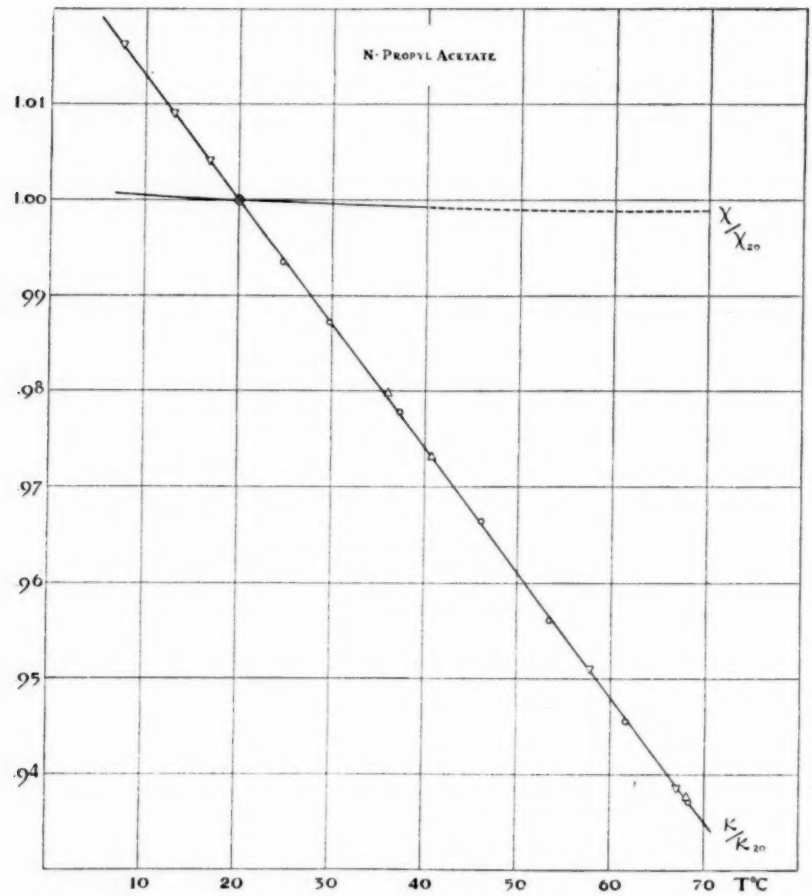

FIG. 3.

magnetism with $(1/\chi_{20})(\Delta\chi/\Delta T)$ very close to 0.00005 in each case. The dotted line in the case of propyl acetate indicates that the densities have been extrapolated (see below). Butyl and amyl acetate, on the other hand, show an increase in diamagnetism above 20°—slight for butyl and appreciable for amyl. The indication is that within the temperature range of these experiments there is a very slight temperature dependence of the mass susceptibility that increases for the higher members of the series, which is in accord with the findings of Cabrera and Fahlenbrach for the alcohols. However, in no case does the variation of χ exceed 0.2 percent.

The Absolute Susceptibilities

The absolute susceptibilities, volume, mass, and molecular (computed on the basis of $\chi = 0.720 \times 10^{-6}$ for water) are given in Table II and are shown graphically in Fig. 5. In each case the volume susceptibilities represent the mean of from four to eight independent observations. The curve labeled χ_M indicates the agreement with Pascal's law of the additivity of atomic susceptibilities. The general formula for the alkyl acetates may be written $HCH_3CO_2(CH_2)_n$, with $n=1$ for methyl, $n=2$ for ethyl, etc. If the atomic susceptibilities are strictly additive a plot of the molecular susceptibility of each acetate against n should be a straight line of the form:

$$(\chi_M)_n = (\chi_M)_{\text{Ac. acid}} + n(\chi_M)_{CH_2},$$

that is, a straight line having a slope equal to the molecular susceptibility of CH_2 and an intercept on the ordinate equal to the molecular susceptibility of acetic acid. The values for CH_2 and acetic acid in Table II have been computed from the acetate susceptibilities by the method

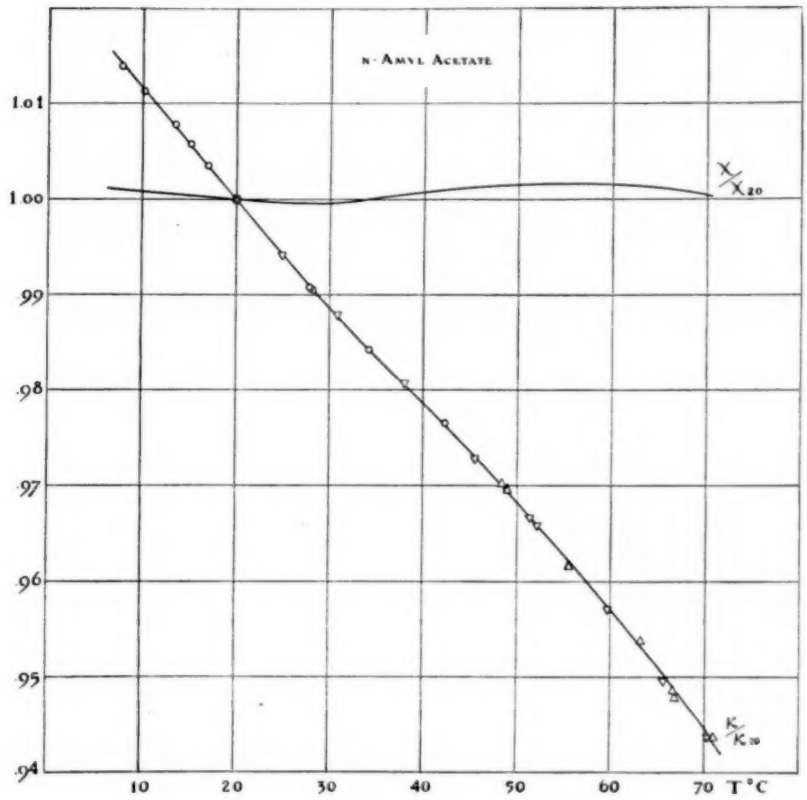

FIG. 4.

TABLE II.

	B.P.†	Mol. Wt.	Density (20.7°)	$-\kappa_{20.7}\cdot10^6$	$-\chi\cdot10^6$	$-\chi_M\cdot10^6$	$-\Delta\chi_M\cdot10^6$	$-\chi\cdot10^6$ (other authors)
Methanol CH_3OH	64.6	32.03	0.7907	0.5289	0.669$_6$	21.42		0.683 (P) 0.650 (I) 0.674 (CF)
Methyl acetate $C_3H_6O_2$	56.6–56.9	74.05	0.9328	0.5320	0.570$_2$	42.23	−0.04	0.590 (P) 0.586 (B)
Ethyl acetate $C_4H_8O_2$	76.7–76.9	88.06	0.8997	0.5515	0.613$_0$	53.98	0.00	0.627 (P) 0.608 (I) 0.621 (B)
n-Propyl acetate $C_5H_{10}O_2$	101.4–102.0	102.08	0.8855	0.5704	0.644$_2$	65.75	0.06	0.646 (B)
n-Butyl acetate $C_6H_{12}O_2$	126.4–126.6	116.09	0.8804	0.5840	0.663$_2$	77.00	−0.40	
n-Amyl acetate $C_7H_{14}O_2$	148.0–148.4	130.11	0.8735	0.5979	0.684$_5$	89.06	0.05	
Acetic acid $C_2H_4O_2$		60.03	1.0485	0.5338	0.509$_1$	30.56*		0.526 (P) 0.535 (CF) 0.520 (S) 0.534 (K) 0.528 (B)
CH_2						11.67*		$-\chi_M\cdot10^6$ 11.86 (P) 11.36 (B) 11.48 (CF) 14.5 (Bi)

* Computed.
† The boiling points have not been corrected for barometric pressure.
(P) P. Pascal, Ann. de chim. et phys. (8) **19**, 5 (1910).
(I) T. Ishiwara, Sci. Rep. Tôhoku Univ. **3**, 303 (1914).
(CF) B. Cabrera and H. Fahlenbrach, Zeits. f. Physik **85**, 568(1933); **89**, 682 (1934).
(B) S. Bhatnagar *et al.*, Phil. Mag. **18**, 449 (1934).
(S) Alpheus W. Smith and Alva W. Smith, J. Am. Chem. Soc. **40**, 1218 (1918).
(K) K. Kido, Sci. Rep. Tôhoku Univ. **21**, 149 (1932).
(Bi) F. Bitter, Phys. Rev. **33**, 149 (1932).

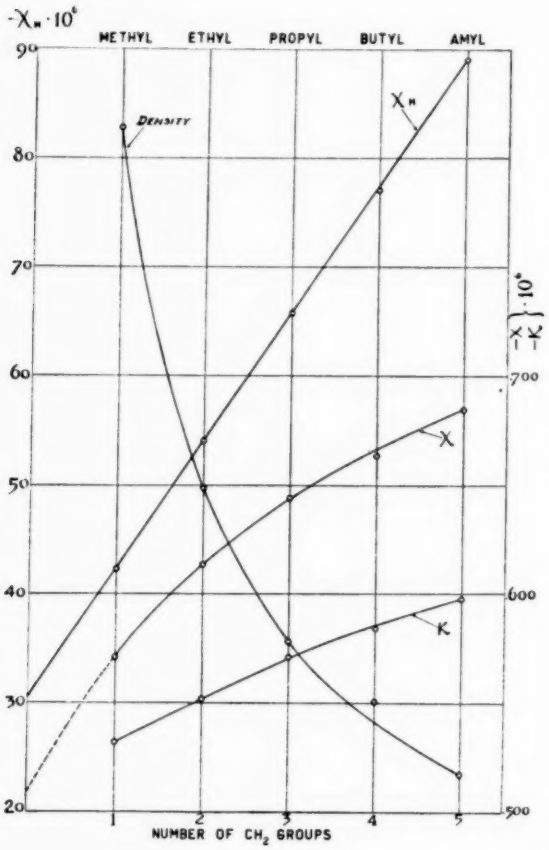

FIG. 5.

of least squares and the χ_M curve drawn accordingly. In this computation, however, butyl acetate was not included because of its apparently irregular position in the series as revealed in each of the curves in Fig. 5. This irregularity is most striking in the case of the densities.[16] (No ordinates have been indicated for the density curve; it merely indicates relative values at 20.7°.) As a matter of fact, the values for CH_2 (-11.68×10^{-6}) and for acetic acid (-30.60×10^{-6}) obtained if butyl acetate is included differ little from those in the table, but the curve fits by no means as well, the average deviation of the points being more than doubled. For the curve as drawn this deviation does not exceed 0.1 percent. The actual deviations are given in the column $\Delta\chi_M$.

In view of the temperature variation of χ the question of the agreement with Pascal's law at higher temperatures arises. A computation made for 50°, omitting methyl acetate, which was not measured at this temperature, gives -11.72×10^{-6} and -30.45×10^{-6} for CH_2 and acetic acid with about the same scattering as before, which would indicate a decrease in the diamagnetism of acetic acid with temperature of about the same order as the first three acetates and an increase with temperature of the diamagnetism of CH_2.

DENSITIES

The densities used in computing the mass susceptibilities of methanol, methyl, ethyl and propyl acetates were taken from the *International Critical Tables*. For methanol and ethyl acetate these are in good agreement with values reported in 1930 by the Bureau International d'Étalons Physique-Chimique.[17] For propyl acetate the equation in the *I.C.T.* is limited to the range 0°–40°C and the probable error is put at 0.001. Young's values[18] for propyl acetate extend well beyond the 70° range needed, but his values would give an increase in χ about twice that shown in Fig. 4. The curve as drawn is much more consistent with the behavior of the other acetates.

The densities of butyl and amyl acetates were measured by Miss Mildred Kamner of the Columbia University Department of Chemistry under the direction of Professor V. K. LaMer, using portions of the same material that had been used for the susceptibility measurements. For butyl acetate four determinations were made by pycnometer at 0°, 20°, 50°, 70°C and for amyl acetate five determinations at 0°, 20°, 35°, 50°, 70°C. The equations computed from these results together with the average deviation of the experimental points are:

Density of *n*-butyl acetate from $t=0°$ to $t=70°C$:

$$\rho_t = 0.90151 - 1.01079\times10^{-3}t - 0.380\times10^{-6}t^2 \pm 4\times10^{-5}.$$

Density of *n*-amyl acetate from $t=0°$ to $t=70°C$:

$$\rho_t = 0.89316 - 0.9481\times10^{-3}t - 0.388\times10^{-6}t^2 \pm 6\times10^{-5}.$$

[16] In this connection it is perhaps worth noting that Cabrera and Fahlenbrach found the greatest departure from regularity in the case of butyl alcohol.

[17] J. chim. phys. **27**, 411 (1930).

[18] S. Young, Proc. Roy. Dub. Soc. **12**, 434 (1910).

The densities of butyl acetate agree very well with values computed from Gartenmeister's volume equation.[19] For amyl acetate they differ by about 2 percent although the relative change in density is very nearly the same. The agreement with the results of Lieben and Rossi[20] on butyl and amyl acetate and of Lievens[21] on amyl acetate is by no means so good.

The densities of the neutral solutions in terms of water at 20° were:

For solution neutral *vs.* air at 20.7° $\rho_s\ 20/\rho_0\ 20 = 1.0203$;
For solution neutral *vs.* helium at 20.7° $\rho_s\ 20°/\rho_0\ 20° = 1.01978$ (Miss Kamner).[22]

Discussion of Errors

The important sources of error to be considered in appraising the absolute values given for the volume susceptibilities in Table II are the susceptibility of air, slight variations in the neutral solution in the course of time (this is negligible for the calibrating solutions because of their small nickel chloride content), the difference in surface tension between the organic liquids and the nickel chloride solutions,[23] and finally errors of observation. An estimate of these gives the probable error in the volume susceptibilities as $\pm 0.0009 \times 10^{-6}$, of which observational errors account for about $\pm 0.0003 \times 10^{-6}$.

As for the mass susceptibilities, in view of the uncertainty of the density values and in the absence of chemical tests for purity a fourth figure cannot be regarded as significant.

The figures for the average deviation in the tables of temperature variation may be considered a measure of the precision of these measurements.

[19] Gartenmeister, Lieb. Ann. **233**, 259 (1886).
[20] Lieben and Rossi, Lieb. Ann. **158**, 169 (1871).
[21] Lievens, Chem. Soc. Belg. **33**, 126 (1924).
[22] If the susceptibility of $NiCl_2$ is computed in terms of water from this value of the density (assuming the volume of the solution to be greater than the volume of the water by a factor of 1.00059) the value $\chi = 36.4 \times 10^{-6}$ is obtained, some 10 percent higher than the value of Liebknecht and Wills (33.4) and the more recent values of Fahlenbrach (33.6) and Brant (33.8), though very much less than the 44.7 (undoubtedly too high) of Ishiwara in the I.C.T. Whether or not this difference is significant cannot be stated positively since no chemical analysis of the solution was made.
[23] Since the positions of the two menisci are determined by setting the telescope cross-hairs tangent to the images of the menisci a slight error is introduced if the two menisci have not the same shape.

Conclusion

In the light of the experiments on nickel chloride solutions the suggestion of Cabrera and Fahlenbrach[24] that the anomalous behavior of water reported by Wills and Boeker[2] in their first paper might be accounted for by variation of the nickel chloride in the calibrating solutions must be regarded as incorrect. It is probable that the water results are to be explained as Wills and Boeker suggest[25] by a leakage of air in the helium bulb. Experience with the manometric balance has shown that this behavior is characteristic of a gradual displacement of helium by air in the apparatus.

The measurements of temperature variation show that the first five of the alkyl acetates belong to the large group of organic compounds that show very little variation of susceptibility with temperature. Such electric dipole measurements as have been made on the acetates suggest the same sort of association as exists in the alcohols and it would be interesting to have measurements on the higher members of this acetate series to see if they show the same increasing dependence on temperature as the higher alcohols.

The agreement with Pascal's law is very good —except for butyl acetate. However, comparison of these measurements with the results of other experimenters repeats the picture of conflict generally found in susceptibility data where measurements on the same substance may differ by two or three percent while individually a precision ten times as great is claimed. Attention should be called to Bitter's value for CH_2 obtained from measurements on the gases of the methane series. The 20 percent difference between the values for gases and for liquids is not unexpected in view of the change of state. The measurements of Vaidyanathan[26] on vapor susceptibilities indicate a discontinuity in the susceptibility curve in the change from the liquid to the vapor state for all the substances he measured and the increase in diamagnetism is

[24] H. Cabrera and B. Fahlenbrach, Zeits. f. Physik **82**, 759 (1933).
[25] A. P. Wills and G. F. Boeker, Phys. Rev. **46**, 907 (1934).
[26] V. I. Vaidyanathan, Ind. J. Phys. **11**, 135 (1928).

marked for pentane, hexane, and heptane, but it is unfortunate that the precision of vapor measurements is such as to make any comparison inconclusive.

I wish at this time to express my thanks to Professor A. P. Wills under whose direction these experiments were carried out, to Professor V. K. LaMer for permitting the use of his laboratory for the density measurements, and to Mr. Samuel Seely and Mr. Erwin Watermeyer for their continued assistance in taking measurements.

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The Energy Levels of Inert-Gas Configurations

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THE energy levels for the configuration $n'p^5np$ have been calculated by Shortley,[1] neglecting the electrostatic interaction between the two groups of levels coming from different parents of the ionic doublet. From the matrices of electrostatic and spin-orbit interaction[2] in jj coupling he obtained four secular equations involving six radial integrals. These are a linear, a quadratic, a cubic, and a quartic equation, corresponding to values of $J=3$, 0, 2, and 1, respectively. The solution of the cubic and quartic equations obviously involves a great amount of complicated arithmetic, and consequently in all cases where the electrostatic interaction between the two groups is small, Shortley found that a valid simplification can be made. If this interaction is neglected, the matrices may be reduced, and the cubic and quartic equations split up into linear and quadratic equations.

For small values of n, however, this approximation is no longer valid, and the complete secular equations must be solved. Some work has already been done in this field by Inglis and Ginsburg,[3] and again by Shortley,[4] on the energy levels of the configuration $2p^53p$ of neon I.

The present calculations are an extension of this work and comprise the $2p^54p$ and $5p$ configurations of neon, $3p^54p$ and $5p$ of argon, $4p^55p$ of krypton, and $5p^56p$ of xenon. The six radial integral parameters were first calculated from the observed energies as taken from Bacher and Goudsmit,[5] making use of the linear and quadratic equations and expressions for the sum of the roots of the cubic and quartic. For this work it was found that the two parameters representing the spin-orbit interaction could be combined as follows

$$K=\tfrac{1}{4}(\zeta'-\zeta)$$

and consequently five equations involving five unknowns could be obtained:

$$\begin{aligned}
3a &= -F_0-F_2-2K,\\
0a &= -F_0-2\tfrac{1}{2}F_2+3G_0+K\\
&\quad -[(-2\tfrac{1}{2}F_2+G_0-3K)^2+2(2G_0-5F_2)^2]^{\frac{1}{2}},\\
0d &= -F_0-2\tfrac{1}{2}F_2+3G_0+K\\
&\quad +[(-2\tfrac{1}{2}F_2+G_0-3K)^2+2(2G_0-5F_2)^2]^{\frac{1}{2}},\\
S_3 &= -3F_0+3F_2+12G_2,\\
S_4 &= -4F_0-F_2+4K,
\end{aligned}$$

where S_3 and S_4 represent the sums of the roots of the cubic and quartic equations.

The five parameters thus obtained were substituted in the original cubic and quartic equations and ζ' was then plotted graphically against the energy. This graphical method provided a comparatively simple means of adjusting not only ζ', but the other parameters as well, since the properties of the curve could easily be studied.

After the parameters had been determined by the graphical method, they were finally adjusted

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[1] George H. Shortley, Phys. Rev. **44**, 666 (1933).
[2] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).
[3] D. R. Inglis and N. Ginsburg, Phys. Rev. **43**, 194 (1933).
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[5] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).

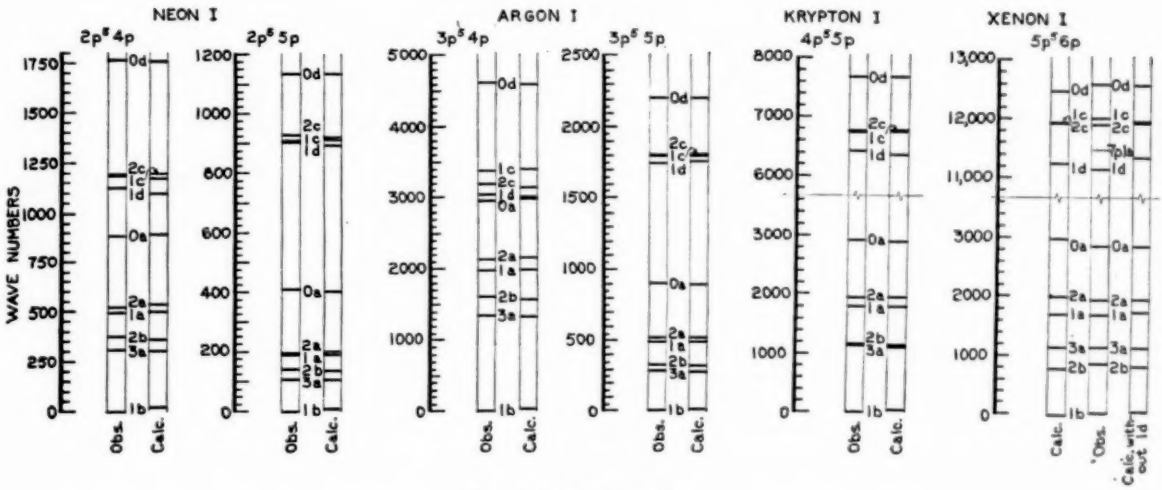

FIG. 1. Energy levels.

TABLE I. *Values of the radial integral parameters.*

	NEON I		ARGON I		KRYPTON I	XENON I	
	$2p^54p$	$2p^55p$	$3p^54p$	$3p^55p$	$4p^55p$	$5p^56p$	without $1d$
F_0	−598.0	−380.7	−1945.0	−794.5	−2950	−4600	−4647
F_2	44.5	18.5	178.0	48.0	175	175	174
G_0	240.0	104.3	695.0	216.5	649	638	610
G_2	12.5	5.7	35.5	12.5	41	30	19
ζ	14.0	5.2	50.0	17.5	156	410	341
ζ'	507.0	515.2	894.0	945.0	3536	6990	7029

by a method of least squares worked out by Shortley.[6]

The best values obtained for the radial integral parameters are given in Table I. Fig. 1 shows the energy levels. The agreement for neon, argon, and krypton is in every case better than that which has been obtained for the $2p^53p$ configuration of neon,[6] the maximum error for neon $5p$, which agrees best, being only 12 cm^{-1}. The agreement in the case of xenon is less satisfactory because of perturbations by the lower group of the $7p$ configuration. Shortley found that if he chose the $1a$ level of the $7p$ group in place of the $1d$ level already assigned, a much better agreement could be obtained. In the present calculations no definite reassignment was made. Instead, all the levels except the $1d$ were readjusted by least squares, the $1d$ level being allowed to fall where it might. The result is shown in the column marked "calc. without $1d$." The agreement here is seen to be greatly improved, the maximum error being reduced to half its former value. In the column of observed levels, the $1a$ level from the $7p$ configuration is shown by a dotted line.

I am grateful to Professor C. W. Ufford for assisting me with this work.

[6] George H. Shortley, Phys. Rev. **47**, 295 (1935).

The Energy of Formation of Negative Ions in O_2

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(Received June 17, 1935)

This paper reports the results of an attempt to evaluate the energy of attachment of electrons to molecules in O_2, by determining at what energy the electron is detached from the O_2 ion in impact with molecules. A value of 0.34 volt is found. In this investigation the complicated phenomena reported by Cravath and Bradbury as a function of the potentials of the high frequency fields employed in the Loeb electron filter, are investigated and explained. At the proper frequencies and with uniform fields electrons can effectively be filtered out without material ion capture. At higher fields the negative ions break up leading to an increased capture of carriers. If many free electrons are present at about the first radiating potential in O_2 (8 volts of energy) at high frequencies photoelectrons liberated at the wires and escaping capture may cause an increase in the current through the filter, especially at higher pressures ("hump effect" of Cravath). Finally at very high fields and especially at higher pressures the electrons ionize by impact producing an increase in current followed by a rapid decline due to capture. Shortly thereafter an arc breaks. At the highest pressures studied (20–60 mm) reattachment of electrons masks all the phenomena and a spark breaks very shortly after a rise of current is observed. The ions have been shown to break up in an X/p (field strength in volts/cm, pressure in mm of Hg) of 90. This corresponds to an ion energy of between 0.136 and 0.68 volt with the higher value the more likely. Of this only about half is available for electron detachment so that one can set 0.34 volt as the probable upper limit of the attachment energy which might correspond to a wavelength of 36,000A.

EVER since it has been clearly recognized that free electrons attached themselves to molecules to form negative ions it has been the goal of investigators to learn something of the nature of this process. The early experiments of Franck,[1] and of Wellisch,[9] the theory of J. J. Thomson[2] and the later researches of Loeb,[3] Wahlin,[4] Bailey[5] and his collaborators, Cravath,[7] and finally the beautiful papers of Bradbury[6,8] have given some indication as to the molecular and atomic types attaching electrons and as to the probability of attachment as a function of electron energy. Of the gases investigated by Bradbury *apparently* only two gases attach electrons with the emission of radiation,* to wit, O_2 and SO_2. All other processes are of a nature where the energy of attachment can be removed by a third body. As to the heat of formation of these ions nothing is known. The observation of even atomic recombination spectra is so difficult that all too little is known of these processes. All attempts to observe the so-called "electron affinity spectrum"[10] of *atoms* or molecules have thus far proved futile. It is in fact quite unlikely that any progress can be made in this line of attack in the near future for the radiation in O_2 if emitted will be in the infrared and conditions for intense radiation from ion formations require high electron densities in a gas at considerable pressure with very low electron energies, a set of conditions which are more or less mutually exclusive.

Both Cravath and Bradbury, who investigated attachment probabilities using Loeb's electron filter, observed at high alternating field strengths between the grid wires of their filters, a decrease in the transmitted current as the applied alternating field increased. Since *ions* are not captured by the grids at the frequency used, the interpretation made by them was that in such fields the negative ions were accelerated to energies sufficiently great to enable them to knock off their electron in impacts with molecules. The electrons were then captured by the grid wires. Bradbury estimated the energy as about 0.6

* Bradbury and F. Bloch have been investigating this question wave mechanically and though results are not complete the work up to the present makes a radiative process seem unlikely.

[1] J. Franck, Verh. Deutsch, Phys. Ges. **12**, 291, 613 (1910); Pohl, ibid. **9**, 194 (1907).
[2] J. J. Thomson, Phil. Mag. **30**, 321 (1915).
[3] L. B. Loeb, Phys. Rev. **17**, 89 (1921); Phil. Mag. **8**, 98 (1929); **43**, 230 (1912); J. Frank. Inst. **197**, 45 (1922).
[4] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).
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[6] N. E. Bradbury, J. Chem. Phys. **2**, 829, 835, 840 (1935).
[7] A. M. Cravath, Phys. Rev. **33**, 605 (1929).
[8] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).
[9] E. M. Wellisch, Phil. Mag. **31**, 180 (1916); **34**, 33 (1917); Am. J. Sci. **44**, 1 (1917).
[10] O. Oldenburg, Phys. Rev. **43**, 534 (1933).

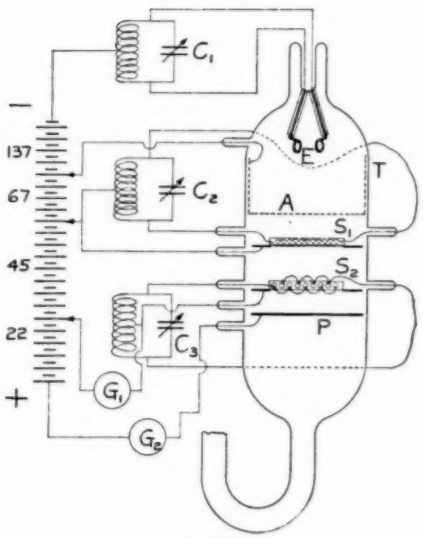

FIG. 1.

volt in O_2. Inasmuch as in neither Cravath's[7] nor Bradbury's[8] measurements uniform fields obtained, an attempt was made to study the phenomenon under better conditions. The apparatus is as indicated in Fig. 1. Inside the tube T a high frequency arc of 10^5 cycles at from 1000 to 5000 volts was operated by resonance from the condenser and coil C_1, across the platinum ring electrodes E. The electrons and ions were driven by a potential of 137 volts across a 5 cm gap through the gauze A. Between A and the filter S_1, 3 cm away, 67 volts drove the ions and electrons to and through the filter. This consisted of alternate 0.2 mm wires 2 mm apart connected to the tuned oscillator C_2. The frequencies used varied from 1×10^6 cycles to 3×10^6 cycles and the potential across the wires was varied by varying the coupling between primary oscillator and C_2. It could be read on a quadrant electrometer used as voltmeter. Three cm below S_1 at S_2 there was a second system of insulated parallel wires denoted as the "smasher." The copper wires were 0.317 cm in diameter with 0.3 cm between the adjacent surfaces (i.e., axes 0.617 cm apart). These were alternately connected to two sides of the oscillator C_3 which was 45 volts positive to S_1. Frequencies of 10^6, 3×10^6 and 10^7 cycles were used here. The smasher potential was varied by coupling as before and the potential was again read on an electrometer. A galvanometer G_1 could be inserted between C_3 and the batteries. At 2 cm below S_1 was a collector plate P at 22.5 volts above S_2 and connected to the positive end of the battery through the galvanometer G_2. The gas used was tank oxygen which had been passed through a purifying train and had been stored in contact with P_2O_5. The purity of the O_2 within the limits assured by that treatment appeared to make little or no difference in the results. The pressures found to be of interest ranged from 2 to 20 mm of Hg and were read on a specially constructed McLeod gauge.

The mixture of ions and electrons generated by the arc was driven by the fields to the filter S_1. Here a transverse high frequency alternating potential between the parallel wires of about 60 to 70 volts swept out the greater portion of the electrons of high mobility, letting the ions through. In the field of the smasher of which the high frequency alternating potential could be run from 10 up to 1000 volts by varying the coupling, and the power output from a push pull neutralized amplifier, the ions could be accelerated to speeds at which they would shed their electrons. While the field between the grid wires was not uniform it was sufficiently uniform compared to those of Bradbury and Cravath to enable some conclusions to be drawn. At the surface of the smasher wires the field X was 1.318 V/d (V potential, d wire spacing), in the center of the field it was 0.879 V/d, by calculation. Measurements on an electrolytic model gave 1.33 V/d and 0.835 V/d, respectively, with a field of 1.2 V/d about 0.1 d from the surface of the grid. The current of ions escaping smashing or capture at the smasher were received by plate P and registered as a current through the galvanometer G_2. The galvanometer G_1 gave the current captured by the smasher. A decrease in the current through G_2 with an increase through G_1 indicated capture by the smasher of ions or electrons. An increase in both currents denoted production of negative ions in the smasher field. Measurements of the current through G_2 were made for pressures from 2 mm to 60 mm as a function of the potential across S_2 for frequencies of 10^6, 3×10^6 and 10^7 cycles.

The highly complicated curves are shown in Figs. 2, 3 and 4 at three characteristic pressures

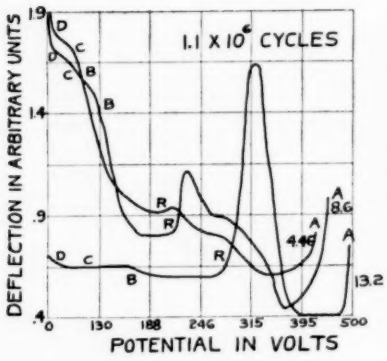

FIG. 2.

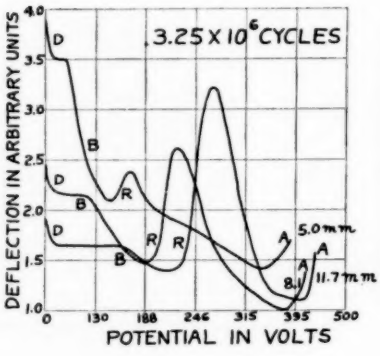

FIG. 3.

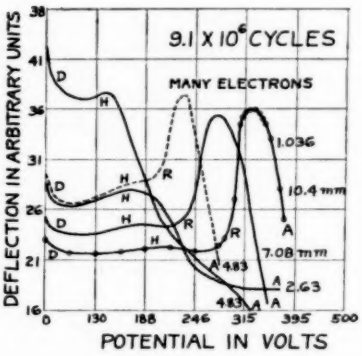

FIG. 4.

expressed in mm of Hg and for the three frequencies. The galvanometer deflections are in arbitrary units and the scales are not the same for the curves at different pressures. It is to be noted that the origin of ordinates in these curves in no case indicates zero current. At best the deflections at ion break-up never dropped much below about half the initial current due to secondary ionization at high fields, as will be seen. The abscissae are in volts as indicated, the scale being uneven since for these curves it sufficed to plot the potential in terms of electrometer readings which have been converted to volts from calibration curves. There are certain important features of the curves designated by letters; *viz.* *A*, arc breaks; *R*, sharp rise in current; *H* (in high frequency curves only), designating a "hump effect" of Cravath, *B* (in lower frequency curves only) indicating ion breakup, *C* (in lowest frequency curves only), indicating *ion* capture by grid, and *D*, decline of the curves due to capture of some free electrons not removed by the filter. In Fig. 5 are plotted the early parts of the curves for G_1 (dashed) and G_2 (full) for 3×10^6 and 10^7 cycles at the pressures indicated. They show the true character of events indicated by *B* and by *H* as will be seen.

The interpretation of the events indicated by the letters will now be given.

A represents the breaking of an arc or glow discharge between the smasher wires as was evidenced not only by large changes in current but by visual observation. At times, careful increase in smasher potential led to step-like increases in the current through G_2 accompanied by one pair, two pairs and three pairs of the wires exhibiting arcs or glow discharges between them. The plots of arcing potential *versus* pressure for the curves at 10^7 and 3×10^6 cycles are given by the observed points *AII* and *AL* in Fig. 6. Why the arcing potentials were always lower for the high frequency *AII* as well as being more uniform is not clear, except that at the higher frequency there were always plenty of free electrons which had not been captured by the electrodes so that the potentials were not capricious due to time lags as at lower frequencies *AL*.

The rise *R* common to all curves can unquestionably be attributed to a very intense ionization by electron impact due to energy gained in the smasher field. It was always greater the less the chance for capture of free electrons by the grid, i.e., at higher pressures. The value of the potential at *R* as a function of the pressure is shown in the two curves *RH* and *RL* of Fig. 6 for high and low frequencies, respectively. The high frequency potentials are higher for this phenomenon than the low frequency since presumably the electrons could no longer get their full terminal energy in one half-cycle at 10^7 cycles and hence the rate of gain of energy to cause *R* demanded higher fields. It may appear strange that any increase should be observed in the curves since electron capture by the electrodes is occurring at these fields. It does tend to disappear below 4 mm. However, the electron mobility varies inversely with the average electron energy and thus as the electrons approach 14 volts energy in the field before ionizing the chance of capture by the grid is not increased proportionally to the

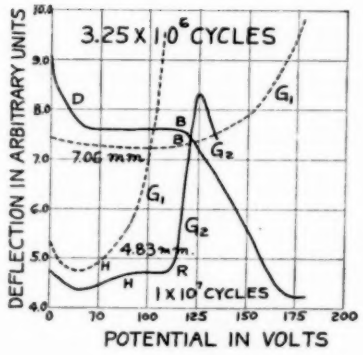

FIG. 5.

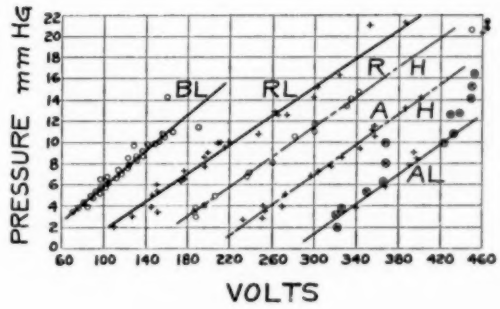

FIG. 6.

field. Thus the rate of gain of current by ionization by collision may outweigh the rate of capture. When all electrons get the ionizing energy in one half-cycle and produce new electrons, thus having their average energies reduced by inelastic impacts, their mobilities go up and an increased capture occurs. This causes the decline, which, however, never reaches zero and is converted to a current increase again as an arc breaks. There are in fact indications of other critical potentials in the declines of many of the curves.

In the high frequency curves the sharp rise is preceded by a small rise and a subsequent decline. It is observed chiefly at the higher frequency and is particularly prominent with inadequate filtering, i.e., with many free electrons reaching the grid. It is the "hump effect" observed by Cravath and as the curves for the currents through G_1 and G_2 of Fig. 5 show, it is clearly an *increase of current due to an increase* in *electrons created at* S_2. It is quite possible that it is due to liberation of photoelectrons at the smasher wires which can escape capture at high frequencies. They come from radiation due to the free electrons present receiving energy enough to excite the first radiating potentials of O_2. The hump is not prominent at higher pressures, and disappears at all lower frequencies where electron capture by the grids is effective.

The curves at 3×10^6 cycles all show a sharp break B, which is shown also at 1×10^6 cycles as a sharp increase in slope. This is masked by the "hump effect" at 1×10^7 cycles. It is also probable that at 1×10^7 cycles at these pressures the chance of an ion making an impact with a neutral molecule in one half-cycle becomes small so that the efficiency of break-up is diminished. A graph of this break-up to larger scale in the upper curves of Fig. 5 shows that at B the current through G_2 decreases while that through G_1 increases. The percentage changes do not appear to be equal as the galvanometer sensitivities are not the same and as the current through G_1 is initially greater than that through G_2. This means that we are observing a sudden increased capture of ions at S_2. This can only be due to an ion break-up in the smasher field, with subsequent capture of free electrons knocked off from the negative ions. The values of the potentials at B taken from the break points on the curves at 3×10^6 and 1×10^6 cycles when plotted against pressure give the line BL in Fig. 6. It is seen that they lie on a fairly smooth straight line.

At the lowest frequencies the initial drops due to D are followed by a continual decline C which appears more marked at lower pressures. Actually the rate of decline is probably the same and appears more prominent only due to the much larger currents observed at the lower pressures. This decline is undoubtedly due to a *capture* of some of the *ions* at the lower frequencies by the grid, and mobility studies bear this out. Calculation shows that capture of ions is probably negligible at 3×10^6 cycles while it begins to be important at 1×10^6 cycles, for if mobilities are normal the ions will move 0.08 of the distance between wires in one half-cycle.

The initial decline of all curves D is marked at the lower pressures and is undoubtedly due to the capture of some electrons by the lower potentials at S_2 which had escaped capture due

to the weaker fields at S_1. They are of no significance. At pressures much lower than 2 mm all curves show an almost monotonous decline at different rates for different frequencies due to the efficient capture of electrons by the grid. Collisions of electrons with the molecules in the space between wires begin to be so infrequent as to permit the escape from attachment to form ions of newly created electrons which produced the effects observed above. At pressures above 20 mm the electrons produced by processes below the ionization potential in most cases attach to molecules and thus the currents observed are nearly constant or increase slightly until the point R is reached. As with increasing pressure at these distances the arcing field strength is lowered we usually get an arc before the current increases much beyond R.

Since the potentials at which the various features A, R and B of these measurements occur vary linearly with pressure even though they do not pass accurately through the origin in the ranges studied the values of the field strengths and ratios of field strengths to pressure may be calculated to a sufficient degree of approximation for any one point of the line conveniently chosen in the region of reliable measurement and are characteristic of the process involved. At $p=7.6$ mm the values of the potential at which the phenomena are observed may be tabulated as in Table I. The quantity V/d is the field strength for a uniform field. $(X)_{0.1}$ is the field at 0.03 cm from a wire of S_2 where we can expect the phenomena to begin to be important, here $(X)_{0.1}=1.2\ V/d$. $(X)_{0.1\ max.}$ is the *peak* value of the field and these quantities divided by $p=7.6$, the pressure in mm, gives the parameter of interest. Max. k is the factor k by which the electron energy exceeds that of thermal agitation at 0°C in a given potential field. The data of

TABLE I.

Event	V	V/d	$(X)_{0.1}$	$(X)_{0.1\,max.}$	$\frac{(X)_{0.1}}{p}$	$\frac{(X)_{0.1\,max.}}{p}$	max. k
B	120	400	480	680	63	89.5	200
RL	183	610	732	1035	96.5	137	—
RH	245	815	980	1380	128	181	—
AH	310	1033	1250	1770	165	233	—
AL	385	1283	1540	2180	203	287	—

Brose[11] on O_2 permit us to obtain an extrapolated value at $(X/p)_{0.1\ max.}$ of about 220 in the case of B. This means that the *electron* energy is about 7.8 volts in the fields where the break-up of negative *ions* begins. While it is not safe to extrapolate Brose's curves for electron energy too far one can say that as the curve for k as a function of X/p is nearly linear at high fields, the electron energy at $(X/p)_{0.1\ max.}=137$ (where the electrons ionize), allows us to place k at R as of the order of 300. This represents an electron energy of about 10 volts. This value is of the order of magnitude of the energy required to ionize the O_2 molecule (14 volts). It may further be added that the electron energy at the beginning of the hump in the "hump effect" is again of the order of 8 volts which is near that of the first radiating potential of O_2. Thus at high frequencies where electron capture is inefficient the "hump effect" may be caused by a photoelectric liberation of electrons from the grid wires of S_2.

As regards the *actual energy* of the *negative ions* when the ion begins to lose its electron probably little more definite can be said than that this phenomenon occurs closely in the neighborhood of an $X/p=90$. While the general break-up will occur when the root-mean-square field reaches the break-up value, the *beginning* of the break in the curve which is here recorded will occur when ions as far away as the distance of travel in one half-cycle from a grid wire *begins* to break up. Hence $(X/p)_{0.1\ max.}$ is the value selected as leading to an evaluation of the energy of attachment. It is unfortunate that one cannot estimate the average energy of a *negative ion* in a field of this value. Because of persistence of velocity the ion will gain its energy over several free paths and thus the energy cannot be calculated. Its large gain will, however, be in the first free path and at best will be of the order of twice that in one path. Furthermore the free path of an ion is not known when X/p is high. The *normal ion* in O_2 has a free path of the order of 0.2×10^{-5} cm at N.T.P. It is conceivable that at an $X/p=90$ the path could nearly be that of an O_2 *molecule* as the attractive forces between ions and molecules here may become inappreciable.

[11] H. L. Brose, Phil. Mag. 1, 536 (1925).

Evidence for such increases in the case of ions of high energy is given by Mitchel and Ridler[12] and by Ramsauer and Beeck.[13] Hence one can, assuming that the energy is gained in one free path, set the energy of the ion as about $X\lambda$, i.e., the potential existing across an ionic free path in the direction of the field. This yields 0.68 volt for $\lambda=1\times10^{-5}$ cm and 0.136 volt for $\lambda=0.2\times10^{-5}$ cm. Considering persistence of velocity and the probability that λ has begun to increase in this region the upper figure seems the more probable. Again it must be remembered that in ion impact with a molecule the total energy above is not all available for detachment for some must go to conserve momentum, which in this case means that only half of the 0.68 volt is available for detachment. Hence we can conclude that the *electron when it attaches to an O_2 molecule in general does not liberate much more than 0.34 electron volt of energy.* Thus the red limit of a continuous attachment spectrum would lie at 0.34 volt and since Bradbury has shown that attachment becomes small for electrons of 0.4-volt energy it is clear that a continuous electron affinity spectrum must be looked for between 36,300A and 15,800A, and it might possibly be in still longer wave-lengths. As at present there seems to be no way of accurately fixing the energy of an ion in O_2 in a field where $X/p=90$ these limits must for the present suffice.

In conclusion the writer desires to express his thanks to Mr. Fred Ludecke who was sent to him by S.E.R.A. to help in this work, and without whose assistance some of the data could not have been taken, to Dr. A. M. Cravath for his calculations of the value of the smasher field, to Professors N. E. Bradbury and O. Luhr for their valuable discussions in connection with this work and to Dr. L. C. Marshall for the design of the oscillators used.

[12] Mitchel and Ridler, Proc. Roy. Soc. **A146**, 911 (1934).
[13] Ramsauer and Beeck, Ann. d. Physik **87**, 1 (1928).

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On the Mechanism of Unimolecular Electron Capture

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The formation of negative ions by electron capture in gases in which a dissociation process does not occur is explained by a unimolecular process involving the excitation of molecular vibrational levels and subsequent loss of energy by collision or resonance. In order to obtain a proper order of magnitude to agree with experimental observations, one must assume a change of only one vibrational quantum number. This sets an upper limit on the electron affinity. For the case of O_2, this limit is 0.17 volt consistent with other observations. The theory also yields a dependence of the phenomenon on the average energy of the electrons which is in agreement with experiment.

1. INTRODUCTION

IT is an experimental fact that if a current of free electrons be sent into certain gases, a more or less rapid change in the character of the carriers of negative electricity occurs. This change is one from a high mobility and high random velocity of agitation to drift velocities a thousand-fold smaller. Such a change must be associated with a change from electronic carriers to carriers of at least molecular dimensions. There occurs, therefore, a capture process in gases wherein initially free electrons become attached to neutral molecules forming stable negative ions. The experimental aspects of this process of electron capture and negative ion formation have been studied in some detail,[1, 2] and some of the important characteristics of the phenomena may be briefly summarized.

If the capture process is a random one as the electrons drift through the gas, then a *capture*

[1] N. E. Bradbury, Phys. Rev. **44**, 883 (1933); J. Chem. Phys. **2**, 827 (1934).
[2] V. A. Bailey, Phil. Mag. **10**, 145 (1930).

cross section, σ_c, may be defined such that the loss of free electrons in going a distance dx in the direction of the applied field is given by

$$dI = -I\sigma_c N v_0 / W dx. \quad (1)$$

In this equation I is the free electron current, N, the number of molecules per unit volume, W the drift velocity, and v_0, the average speed of agitation. In actual practice a quantity h is often used. This is the so-called probability of capture at a collision and is defined by $h = \sigma_c/\sigma_R$ where σ_R is the Ramsauer cross section. The result of (1) is an exponential absorption of free electrons as they attach to neutral molecules thereby forming negative ions.

The quantity h varies in magnitude both with the nature of the gas and with the quantity X/p, the ratio of field strength to pressure. This latter quantity is closely related to the average energy of the electrons in the gas, and hence the probability of capture appears to be a function of the average energy of the electrons. In general one finds three widely varying types of behavior in different gases. The first of these may be characterized by the fact that no negative ion formation is observed at any electronic energy and can be explained by the absence of an electron affinity. Such cases are found in the rare gases, nitrogen, hydrogen, and CO_2. In the second case, negative ions are only formed by sufficiently high energy electrons such that dissociation of the molecule can occur. Examples of this are found in N_2O, NH_3, and HCl. Finally, there are gases in which electrons of very low velocity can be captured, and in fact show a decrease of the cross section with increasing electronic energy.

With few exceptions, the value of h seems to be largely independent of pressure for pressures greater than a few mm of Hg. There is qualitative evidence,[3] however, that the probability of capture in oxygen decreases with decrease in pressure below 2 mm, and a strong variation with pressure is observed in NO.

The general phenomena of negative ion formation in most cases are fairly well established. There remains, however, the necessity of discussing the mechanism of the capturing process. A tentative rule has been given for predicting whether or not a given molecule will possess an electron affinity.[4] Granting that this affinity exists, one has to consider the problem of the disposal of the energy which must appear when a negative ion is formed. *A priori* one may consider several possible mechanisms, such as (1) radiation; (2) dissociation; (3) molecular excitation. Let us consider these suggestions in order.

Radiation has been frequently suggested as the form of appearance of the energy. However, the cross sections for such processes have been calculated and are too small by orders of magnitude. In particular Jen[5] has calculated the cross section for capture by radiation of the hydrogen atom (for which the electron affinity is 0.7 volt) and obtains a value of 10^{-22} cm^2 corresponding to an h of the order of 10^{-7}. While this case has not been observed experimentally, the appearance of radiation energy corresponding to the sum of the electron affinity and initial kinetic energy of the electron seems exceedingly improbable.

Electron attachment and simultaneous molecular dissociation resulting in the formation of a negative ion with one of the molecular fragments is of relatively common occurrence with polyatomic molecules. In such cases the energy is carried away in kinetic form by the products of the dissociation. This type of negative ion formation is invariably associated with an increase in the probability of negative ion formation with increasing electronic energy.

This second mechanism apparently does not occur in oxygen or nitric oxide since in these gases an entirely different type of energy dependence is observed, and in addition the electron affinity cannot be as much as the approximately 6 volts necessary to dissociate the molecule. For this case, therefore, we have to consider as a process the excitation of molecular vibration and rotational levels with subsequent loss of energy to other molecules. The theoretical treatment of this means of electron capture will form the subject of this paper and will be treated in the next section.

[3] H. L. Brose, Phil. Mag. **50**, 536 (1925).

[4] N. E. Bradbury, J. Chem. Phys. **2**, 840 (1934).

[5] C. K. Jen, Phys. Rev. **43**, 540 (1933).

2. Theory of Electron-Capture by Molecular Excitation

The capture of an electron by a transition from a free state into a bound state in the molecule and the simultaneous excitation of molecular energy levels is an effect of the weak coupling between electronic and nuclear motion. We will restrict our considerations to the case of diatomic molecules and first ask for the probability of transitions due to this coupling.

Considering the center of gravity of the molecule at rest, we will describe the interaction between electron and molecule by a potential $V(\mathbf{R}, \mathbf{r})$ depending on the position vector $\mathbf{r}$ of the electron and on the vector $\mathbf{R}$ of the relative position of the two nuclei.[6] Let k (standing for three quantum numbers) be a stationary state of the electron at a *given* relative position of the nuclei. The corresponding energy level shall be $E_k(\mathbf{R})$, the normalized eigenfunction $\psi_k(\mathbf{R}, \mathbf{r})$ and the connection between the stationary states, denoted by the same symbol k for different vectors $\mathbf{R}$ shall be that of adiabatic variation of $\mathbf{R}$. Similarly K shall denote the three quantum numbers of a stationary state of nuclear motion under the action of a potential

$$U_k(\mathbf{R}) = U_0(\mathbf{R}) + E_k(\mathbf{R}), \tag{2}$$

where $U_0(\mathbf{R})$ is the potential of nuclear motion for the neutral molecule. The normalized eigenfunction of this state will only depend on $\mathbf{R}$ and shall be denoted by $\Psi_{K,k}(\mathbf{R})$, the energy level by $E_{K,k}$. The equations for the variation of constants will then appear in the form

$$(\hbar/i)\dot{a}_{Kk} = \sum_{K'k'} T_{Kk,K'k'} a_{K'k'}, \tag{3}$$

where $|a_{Kk}|^2$ is the probability of finding the molecule in a state of electronic motion, k, and nuclear motion, K. $T_{Kk,K'k'}$ is the matrix element of the perturbation energy T, which can be easily seen with the above definition of stationary states K, k to be the kinetic energy of the nuclei. The function $U_k(\mathbf{R})$ can be assumed to depend only on the relative distance ξ of the nuclei.[7] Introducing, furthermore, polar angles θ, φ for the direction of $\mathbf{R}$, and calling M the arithmetic mean of the two atomic masses, we can write

$$T_{Kk,K'k'} = \frac{\hbar^2}{M}\int \Psi_{Kk}^*(\xi,\theta,\varphi)\psi_k^*(\xi,\theta,\varphi,\mathbf{r})\left[\frac{\partial^2}{\partial\xi^2}+\frac{2}{\xi}\frac{\partial}{\partial\xi}+\frac{1}{\xi^2}\Delta\theta\right]\psi_{k'}(\xi,\theta,\varphi,\mathbf{r})\Psi_{K'k'}(\xi,\theta,\varphi)\xi^2\sin\theta\, d\theta\, d\varphi\, d\mathbf{r}, \tag{4}$$

where $$\hbar = h/2\pi, \quad d\mathbf{r} = dxdydz, \quad \Delta\theta = \frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

The quantity which is physically interesting is the probability $dP_{KK'}/dt$ that an electron during unit time will make a transition from a free to a bound state associated with a transition $K-K'$ of the molecule. In order to obtain $dP_{KK'}/dt$ from (3), one has to remember that in a gas we have always to deal with a continuous velocity distribution, due to the many though small energy changes from previous collisions with molecules. This is important since going over from the probability $|a|^2$ to $dP_{KK'}/dt$ one has to integrate over a narrow energy range in the neighborhood of that energy, for which $E_{Kk} = E_{K'k'}$. The breadth of this range is given by the lifetime of the final state of the molecule,[8] and if we may assume for simplicity that only *one* bound state of the electron in the molecule is effectively important, this means that for any given molecular transition $K-K'$ only electrons with a very well defined energy can be captured at all.

If $f(E)dE$ is the probability of finding in the stationary distribution an electron within a range between E and $E+dE$ of its kinetic energy and if N is the number of molecules per unit volume one finds thus from (3)

[6] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927).

[7] For bound states k of the electron this is, of course, true. For free states k there is a privileged direction in space, namely, the asymptotic direction of the electrons. Due to the fact that we shall deal only with slow electrons and have E_k small compared to U_0, this effect is quite negligible.

[8] The lifetime of the initial state is practically infinite.

$$dP_{KK'}/dt=(2\pi/\hbar)Nf(E^*)|S_{KK'}(E^*)|^2. \quad (5)$$

$S_{KK'}(E^*)$ in (5) is the same expression as $T_{Kk,\,K'k'}$ in (4) with the difference, that the electronic functions ψ_k of the initial free state are normalized per unit volume and that k has to be taken such that $E_{Kk}=E_{K'k'}$. E^* shall be the kinetic energy of the free electron for which this condition is fulfilled and to replace the index k in (4), we have written $S_{KK'}$ as a function of E^*. The index k' has been omitted with the understanding that it shall always be taken as the symbol, representing the final bound state of the electron. The expression (5) depends then only on K and K' since E^* is also determined by K and K' through the relation $E_{Kk}=E_{K'k'}$.

Instead of the quantity (5) we will introduce the capture cross section σ_c from (1) by the relation

$$dP_{KK'}/dt=v_0(\sigma_c)_{KK'}N,$$

or
$$(\sigma_c)_{KK'}=(2\pi/\hbar v_0)f(E^*)|S_{KK'}(E^*)|^2. \quad (6)$$

$$v_0=\int_0^\infty(2E/m)^{\frac{1}{2}}f(E)dE$$

is the average speed of the electron.

Without knowing more about the electronic eigenfunctions, than that in the bound state the electron will be found within a volume of the molecular dimensions, we can tell from the order of magnitude of σ_c as given by (6) and (4), which excited states K' of the molecule are most likely to occur and how σ_c is affected by the magnitude of the electron affinity.

Instead of the symbol K we will now use three quantum numbers l, m, n, where $l\hbar$ is the angular momentum, m the azimuthal quantum number, and n the number of quanta of the oscillation of the nuclei around their equilibrium position. Ψ_K in (4) is then a product of a tesseral harmonic of the order l, depending on θ and φ and a function of ξ, being very closely the eigenfunction of the nth state of the harmonic oscillator. Unless the de Broglie wave-length of the incident electron is short compared with molecular dimensions, the expansion of ψ_k and $\psi_{k'}$ with respect to their dependence on θ and φ in tesseral harmonics will practically contain only the first few orders; changes of l by a large number are thus most unlikely. Capturing by mere *rotational* excitation could therefore only occur if the electron affinity were of the order of magnitude of the separation of two rotational levels. But at room temperature this would be less than kT and negative ions so formed would be thermally instable. Therefore the main part of the capturing mechanism must lie in *vibrational* excitation. We may for further purposes assume that no changes of l occur at all; we have then merely to remember, that all energy considerations used later on are only valid with an approximate error of the order of magnitude of the ratio of the separation of rotational and vibrational levels, i.e., about 1 percent.

As far as vibrational excitations are concerned, only those terms under the integral (4) contribute that contain derivatives of $\psi_{k'}$; the others vanish due to the orthogonality of ψ_k and $\psi_{k'}$ with respect to the electron coordinates. Among the remaining terms again, those with *first* derivatives in ξ both of $\psi_{k'}$ and $\Psi_{Kk'}$ will prevail. In fact they will stand to those with the second derivatives of ψ_k in the approximate ratio a/δ, where a is a length of the order of molecular dimensions, and δ the amplitude of the vibration. This is due to the fact that each differentiation, with respect to ξ, acting on $\psi_{k'}$ will give a new factor $1/a$ in the expression (4), since $\psi_{k'}$ both as function of $\mathbf{r}$ and ξ varies essentially over regions of molecular magnitude, while $\Psi_{K'k'}$ as function of ξ will essentially vary over the much smaller region δ. This means physically, that the velocity of the nuclear motion will be so much smaller than that of the electron in its bound state that only terms linear in the nuclear velocity have to be considered. In order to see the dependence of σ_c on the number of excited quanta, it is convenient to expand $\psi_k^*\partial\psi_{k'}/\partial\xi$ in terms of $\Delta\xi=\xi-\bar{\xi}$ around the equilibrium position $\bar{\xi}$ of the two nuclei. Due to the selection rules of the harmonic oscillator, changes of n by the amount $n'-n=\Delta n$ can only occur by terms with at least the $(\Delta n-1)$ power in $\Delta\xi$. But each following power of $\Delta\xi$ diminishes the expression (4) by a factor of the order of magnitude δ/a. At room temperature there will practically be no thermal vibrational excitation, thus $n=0$. Neglecting the dependence of S on E^* (which is certainly justified for sufficiently slow electrons) and taking into account also that ψ_k^* will not vary rapidly within nuclear dimensions, one obtains

from (6) and (4) for capturing by excitation of the vibrational level n'

$$(\sigma_c)_{n'}=\alpha_{n'}\frac{m}{M}\frac{A^2a^3}{\hbar v_0}\left(\frac{\delta}{a}\right)^{2(n'-1)} f(E^*)$$

$$(n'=1, 2, \cdots), \quad (7)$$

where $\alpha_{n'}$ is a numerical constant of the order of magnitude 1, m, the mass of the electron, and A the electron affinity. The quantity a is connected with A by the equation $\hbar^2/2ma^2=A$ and will be of the order of magnitude of the orbital dimensions of the electron in its bound state, i.e., of molecular dimension. This follows from the fact that the binding energy A and the average kinetic energy may be assumed as being of the same order of magnitude. δ^2 is the mean square of the elongation in the ground state of the nuclear oscillation. Formula (7) gives of course only the right order of magnitude for σ_c, if n' is of the order of magnitude 1.

Since E^*+A is the total energy, lost by the electron in the capturing process and has to be equal to the increase of vibrational energy, we have

$$E^*=n'\hbar\omega-A, \quad (8)$$

where ω is the circular frequency of the oscillation. This quantity must be positive, which means

$$A=n'\hbar\omega-E^*\leqq n'\hbar\omega \quad (9)$$

and gives us an upper limit for the electron affinity A, provided that we can determine n'. We will see in section 3 that this indeed is possible with the help of (7), although this formula tells us only the order of magnitude of σ_c. In fact the smallness of δ/a changes the order of magnitude of σ_c, even for values of n' that differ only by one.

Before going over to the discussion of the empirical results, an important supplementary consideration has to be given. The transition probability (5) does not necessarily mean the probability of a capturing process resulting in a stable ion. After the transition $Kk\rightarrow K'k'$ has occurred, the inverse transition $K'k'\rightarrow Kk$ will always occur unless during the lifetime θ of the excited ion it has had a possibility of transferring its vibrational energy to another molecule in the gas, thus becoming energetically stable. In order to have expression (7) really represent the capturing cross section, it is necessary that the transfer of vibrational energy occur during a time τ, which is short compared to the lifetime θ. Whether this is true or not depends of course on the pressure and temperature of the gas. If $\bar{v}$ is the average velocity of the molecules in the gas and s an effective cross section for transfer of vibrational energy, we have

$$\tau=1/N\bar{v}s=\gamma/P, \quad (10)$$

where γ depends only on the temperature and p is the pressure of the gas. On the other hand, the lifetime θ of the excited ion is pressure independent and given by

$$\theta_{KK'}=2\pi\hbar^4/(2m)^{\frac{1}{2}}(E^*)^{\frac{1}{2}}|S_{KK'}(E^*)|^2.$$

Using the same approximations as for obtaining formula (7), we obtain

$$\theta_{n'}=\frac{(2\pi)^2\hbar^4}{(2m)^{\frac{1}{2}}(E^*)^{\frac{1}{2}}\alpha_{n'}A^2a^3}\frac{M}{m}\left(\frac{a}{\delta}\right)^{2(n'-1)}, \quad (11)$$

which is the lifetime of an ion with vibrational excitation n', before a spontaneous emission of the electron occurs. The condition for the validity of (7) is

$$\theta_{n'}\gg\tau \quad (12)$$

and will be satisfied for different pressure ranges in different gases. It should be noticed that in this case the broadening of the final level of the excited ion, mentioned before, will be mostly due to transfer collisions with other molecules and of the order of magnitude $\hbar/\tau$.

On the other hand, for sufficiently low pressures, one will always come to a region where (12) is no longer satisfied and then the capturing cross section will become pressure dependent. We can give an approximate formula of this dependence by the following simple consideration: Suppose that we know at a given time $t=0$ that the ion is in its excited state, due to a previous electron transition. The probability of having it still in this state after a time t will be given by $e^{-t/\theta}$. On the other hand the probability of making a transfer collision after a time between t and $t+dt$ has elapsed is given by

$e^{-t/\tau}dt/\tau$. The total probability therefore that an excited ion makes a transfer collision is

$$\rho = \int_0^\infty e^{-(t/\theta + t/\tau)}dt/\tau = \theta/(\theta+\tau),$$

or since τ is inversely proportional to the pressure p

$$\rho = p/(p+p'), \tag{13}$$

where p' is a "critical pressure," for which $\theta = \tau$. Expression (7) has to be multiplied by this factor in order to give the cross section both for high and low pressures. We find finally:

$$(\sigma_c)_{n'} = \alpha_{n'}\frac{m}{M}\frac{A^2a^3}{\hbar v_0}\left(\frac{\delta}{a}\right)^{2(n'-1)} f(E^*)\frac{p}{p+p'}. \tag{14}$$

For $p \gg p'$ this approaches the pressure independent value (7); for $p \ll p'$, σ_c becomes a linear function of the pressure.

3. Comparison with Experiment

In order to compare the theoretical predictions given in the last section with experiment we will first obtain the value of the quantity h, introduced in section 1 that has to be expected. In order to do this we have to assume something about the Ramsauer cross section σ_R since it is not measured for these low velocities. We will expect for sufficiently low velocities that σ_R approaches some constant value of the order of magnitude a^2. This is consistent with the assumption made in section 2, that for low velocities and inside the molecule the wave function of the electron in its initial state will no longer depend on the velocity. Thus we get from (14)

$$h_{n'} = \frac{(\sigma_c)_{n'}}{\sigma_R} = \beta_{n'}\frac{m}{M}\frac{A^2a}{\hbar v_0}\left(\frac{\delta}{a}\right)^{2(n'-1)} f(E^*)\frac{p}{p+p'}, \tag{15}$$

where β' is a new numerical constant, also of order of magnitude one.

The observed order of magnitude of h for O_2 in the pressure independent region is 10^{-4} and we can see now which values of n' would yield such a result. For simplicity we will assume all the energies A, E^*, and E_0 to be of the same order of magnitude. We shall see presently that this is a reasonable assumption. The quantity $f(E^*)$ in (15) will then become of the order of magnitude $1/E_0$. The pressure dependent factor in (15) has here to be taken unity and we get

$$h_{n'} \leqq (m/M)(\delta/a)^{2(n'-1)}. \tag{16}$$

Now obviously $m/M = 0.33\times10^{-4}$ and therefore in order to have (16) of the right order of magnitude, $(\delta/a)^{2(n'-1)}$ must be of the order of magnitude one. On the other hand, δ/a will be about $1/10$ and thus the only value of n' which we can admit is $n'=1$, irrespective of the fact that we can compute only the order of magnitude of h. From this we can immediately draw a conclusion as to the upper limit of the electron affinity. In fact from (9) it follows with $n'=1$

$$A = \hbar\omega - E^* \tag{17}$$

and

$$A \leqq \hbar\omega = 0.19 \text{ ev}. \tag{17a}$$

The numerical value in this inequality is taken from the well-known frequencies of the vibrational bands of the O_2 molecule.[9]

Since we now know n' to be one, we can give a final expression for h, namely,

$$h = \beta\frac{m}{M}\frac{A^2a}{\hbar v_0}f(E^*)\frac{p}{p+p'}. \quad \beta \leqq 1. \tag{18}$$

Aside from the order of magnitude, (18) gives us a definite answer as to the way in which h depends upon the average energy E_0 of the electrons, if the distribution function $f(E)$ is known. The *velocity* distribution function will be of the type $v^2F(E/E_0)$ where F will approach a finite value for small arguments and rapidly drop off for large arguments. Morse has recently

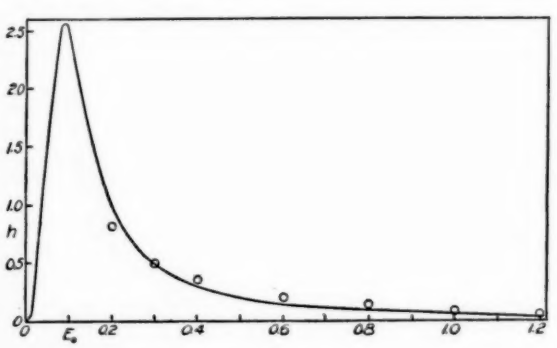

FIG. 1. Probability of capture, h (in arbitrary units) plotted against average electron energy E_0. The circles are experimental points for O_2; the full line, the theoretical curve for $E^* = 0.08$ volt corresponding to an electron affinity of 0.11 volt.

[9] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

shown that $F(E/E_0)$ has the form $F(E/E_0) = e^{-b(E/E_0)^2}$ with $b=0.847$. We will use this function, although its particular form does not materially influence our results. For the *energy* distribution function $f(E)$ we obtain then

$$f(E) = \text{const.}\ (E^{\frac{1}{2}}/E_0^{\frac{1}{2}})e^{-b(E/E_0)^2}. \qquad (19)$$

The factor $E_0^{\frac{1}{2}}$ in (19) has to appear since $\int_0^\infty f(E)dE = 1$. Using (18) and (19) we find for the dependence of h on E_0,

$$h\alpha e^{-b(E^*/E_0)^2}/E_0^2. \qquad (20)$$

In Fig. 1 we have computed such a curve which has been adjusted for $E_0=0.3$ volt, and shown thereon the experimental points. These lie gratifyingly close to the computed curve. There, however, seems to be a systematical deviation in the sense that the theoretical curve rises somewhat too rapidly. This lies probably in the circumstance that we have chosen both for σ_c and σ_R a behavior which they would exhibit in the limit of small velocities. This behavior may not be quite reached at the velocities in which we are interested. The value of E^* which one uses does not greatly influence the character of the curve, particularly for high values of E_0. However, the very fact that there is no experimental indication of h approaching a maximum even for the smallest measured values of E_0 permits the conclusion that E cannot be bigger than about 0.12. Thus from (17) we find also a lower limit for the affinity and we can write $0.07 < A < 0.19$ electron volt. This may be at once compared with some results of Loeb[10] who finds the electron affinity of the oxygen molecule to be definitely smaller than 0.34 volt, in interesting agreement with our requirements.

It is understandable, moreover, why the measurements in O_2 above 3 mm pressure already lie in the pressure independent region. The requirement for such a behavior as stated in section 2 is $\theta \gg \tau$. Taking (11) for $n'=1$, and estimating its order of magnitude in the same manner as was done for h, we obtain $\theta \leqq 10^{-10}$ sec. If we would take in (10) for s the values of the cross section as observed in ion mobilities, we would find $\tau \leqq 10^{-9}$ sec.[11] This indicates that s has to be 10–100 times the collision cross section of the unexcited ion in order to have the requirements fulfilled. Now one has to consider that transfer of vibrational energy from one molecule to another will occur by resonance, even if they are separated by a distance considerably greater than their linear dimensions. This value of s is therefore a most reasonable one.

One must further note that for air at pressures of several mm, one does not yet observe a pressure dependence.[12] This is entirely compatible with the values of s above, although the relative number of other oxygen molecules with which the resonance condition is fulfilled is five times less than in pure O_2. Moreover, for very low pressures in oxygen there are qualitative indications of a decrease in the value of h, as must be expected from this theory. Such a behavior should also occur in air at somewhat higher pressures, but measurements in the region of low pressures are extremely difficult and have not been carried out.

Nitric oxide is the other diatomic gas observed which shows a dependence of h on E_0 similar to oxygen. Since the qualitative conditions for electron capture by molecular excitation will not be very different from those of oxygen, it is very likely that the same explanation will hold. In a similar fashion as in oxygen one may restrict the electron affinity to values less than the energy of the first vibrational level, 0.24 ev, and greater than 0.07 volt. It is interesting to notice that here the experiment *does* show a strong pressure dependence. A difference merely in quantitative conditions between NO and O_2 will be sufficient to cause a change in the ratio θ/τ large enough such that for one case the pressure dependence is hardly observable while in the other case it is strongly pronounced.

[10] L. B. Loeb, unpublished results. We are indebted to Professor Loeb for communicating the results of his experiments to us in advance of publication.

[11] This is reasonable in view of the well-known shortening of the mean free path of an ion due to its charge.

[12] A. M. Cravath (Phys. Rev. **33**, 605 (1929)) has observed a pressure dependence in air. The effect was not observed by one of the authors nor by V. A. Bailey, and it is probable that the dependence observed was the result of some experimental peculiarity.

Can Quantum-Mechanical Description of Physical Reality be Considered Complete?

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It is shown that a certain "criterion of physical reality" formulated in a recent article with the above title by A. Einstein, B. Podolsky and N. Rosen contains an essential ambiguity when it is applied to quantum phenomena. In this connection a viewpoint termed "complementarity" is explained from which quantum-mechanical description of physical phenomena would seem to fulfill, within its scope, all rational demands of completeness.

IN a recent article[1] under the above title A. Einstein, B. Podolsky and N. Rosen have presented arguments which lead them to answer the question at issue in the negative. The trend of their argumentation, however, does not seem to me adequately to meet the actual situation with which we are faced in atomic physics. I shall therefore be glad to use this opportunity to explain in somewhat greater detail a general viewpoint, conveniently termed "complementarity," which I have indicated on various previous occasions,[2] and from which quantum mechanics within its scope would appear as a completely rational description of physical phenomena, such as we meet in atomic processes.

The extent to which an unambiguous meaning can be attributed to such an expression as "physical reality" cannot of course be deduced from *a priori* philosophical conceptions, but—as the authors of the article cited themselves emphasize—must be founded on a direct appeal to experiments and measurements. For this purpose they propose a "criterion of reality" formulated as follows: "If, without in any way disturbing a system, we can predict with certainty the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity." By means of an interesting example, to which we shall return below, they next proceed to show that in quantum mechanics, just as in classical mechanics, it is possible under suitable conditions to predict the value of any given variable pertaining to the description of a mechanical system from measurements performed entirely on other systems which previously have been in interaction with the system under investigation. According to their criterion the authors therefore want to ascribe an element of reality to each of the quantities represented by such variables. Since, moreover, it is a well-known feature of the present formalism of quantum mechanics that it is never possible, in the description of the state of a mechanical system, to attach definite values to both of two canonically conjugate variables, they consequently deem this formalism to be incomplete, and express the belief that a more satisfactory theory can be developed.

Such an argumentation, however, would hardly seem suited to affect the soundness of quantum-mechanical description, which is based on a coherent mathematical formalism covering automatically any procedure of measurement like that indicated.* The apparent contradiction in

[1] A. Einstein, B. Podolsky and N. Rosen, Phys. Rev. **47**, 777 (1935).

[2] Cf. N. Bohr, *Atomic Theory and Description of Nature*, I (Cambridge, 1934).

* The deductions contained in the article cited may in this respect be considered as an immediate consequence of the transformation theorems of quantum mechanics, which perhaps more than any other feature of the formalism contribute to secure its mathematical completeness and its rational correspondence with classical mechanics. In fact, it is always possible in the description of a mechanical system, consisting of two partial systems (1) and (2), interacting or not, to replace any two pairs of canonically conjugate variables (q_1p_1), (q_2p_2) pertaining to systems (1) and (2), respectively, and satisfying the usual commutation rules

$$[q_1p_1]=[q_2p_2]=ih/2\pi,$$
$$[q_1q_2]=[p_1p_2]=[q_1p_2]=[q_2p_1]=0,$$

by two pairs of new conjugate variables (Q_1P_1), (Q_2P_2) related to the first variables by a simple orthogonal transformation, corresponding to a rotation of angle θ in the planes (q_1q_2), (p_1p_2)

$$q_1=Q_1\cos\theta-Q_2\sin\theta \qquad p_1=P_1\cos\theta-P_2\sin\theta$$
$$q_2=Q_1\sin\theta+Q_2\cos\theta \qquad p_2=P_1\sin\theta+P_2\cos\theta.$$

Since these variables will satisfy analogous commutation rules, in particular

$$[Q_1P_1]=ih/2\pi, \qquad [Q_1P_2]=0,$$

it follows that in the description of the state of the combined system definite numerical values may not be assigned to both Q_1 and P_1, but that we may clearly assign

fact discloses only an essential inadequacy of the customary viewpoint of natural philosophy for a rational account of physical phenomena of the type with which we are concerned in quantum mechanics. Indeed the *finite interaction between object and measuring agencies* conditioned by the very existence of the quantum of action entails —because of the impossibility of controlling the reaction of the object on the measuring instruments if these are to serve their purpose—the necessity of a final renunciation of the classical ideal of causality and a radical revision of our attitude towards the problem of physical reality. In fact, as we shall see, a criterion of reality like that proposed by the named authors contains—however cautious its formulation may appear—an essential ambiguity when it is applied to the actual problems with which we are here concerned. In order to make the argument to this end as clear as possible, I shall first consider in some detail a few simple examples of measuring arrangements.

Let us begin with the simple case of a particle passing through a slit in a diaphragm, which may form part of some more or less complicated experimental arrangement. Even if the momentum of this particle is completely known before it impinges on the diaphragm, the diffraction by the slit of the plane wave giving the symbolic representation of its state will imply an uncertainty in the momentum of the particle, after it has passed the diaphragm, which is the greater the narrower the slit. Now the width of the slit, at any rate if it is still large compared with the wave-length, may be taken as the uncertainty Δq of the position of the particle relative to the diaphragm, in a direction perpendicular to the slit. Moreover, it is simply seen from de Broglie's relation between momentum and wave-length that the uncertainty Δp of the momentum of the particle in this direction is correlated to Δq by means of Heisenberg's general principle

$$\Delta p \Delta q \sim h,$$

which in the quantum-mechanical formalism is a direct consequence of the commutation relation for any pair of conjugate variables. Obviously the uncertainty Δp is inseparably connected with the possibility of an exchange of momentum between the particle and the diaphragm; and the question of principal interest for our discussion is now to what extent the momentum thus exchanged can be taken into account in the description of the phenomenon to be studied by the experimental arrangement concerned, of which the passing of the particle through the slit may be considered as the initial stage.

Let us first assume that, corresponding to usual experiments on the remarkable phenomena of electron diffraction, the diaphragm, like the other parts of the apparatus,—say a second diaphragm with several slits parallel to the first and a photographic plate,—is rigidly fixed to a support which defines the space frame of reference. Then the momentum exchanged between the particle and the diaphragm will, together with the reaction of the particle on the other bodies, pass into this common support, and we have thus voluntarily cut ourselves off from any possibility of taking these reactions separately into account in predictions regarding the final result of the experiment,—say the position of the spot produced by the particle on the photographic plate. The impossibility of a closer analysis of the reactions between the particle and the measuring instrument is indeed no peculiarity of the experimental procedure described, but is rather an essential property of any arrangement suited to the study of the phenomena of the type concerned, where we have to do with a feature of *individuality* completely foreign to classical physics. In fact, any possibility of taking into account the momentum exchanged between the particle and the separate parts of the apparatus would at once permit us to draw conclusions regarding the "course" of such phenomena,—say through what particular slit of the second diaphragm the particle passes on its way to the photographic plate—which would be quite incompatible with the fact that the probability of the particle reaching a given element of area on this plate is determined not by the presence of any particular slit, but by the positions of all the slits of the second diaphragm within reach

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such values to both Q_1 and P_2. In that case it further results from the expressions of these variables in terms of $(q_1 p_1)$ and $(q_2 p_2)$, namely

$$Q_1 = q_1 \cos\theta + q_2 \sin\theta, \qquad P_2 = -p_1 \sin\theta + p_2 \cos\theta,$$

that a subsequent measurement of either q_2 or p_2 will allow us to predict the value of q_1 or p_1 respectively.

of the associated wave diffracted from the slit of the first diaphragm.

By another experimental arrangement, where the first diaphragm is not rigidly connected with the other parts of the apparatus, it would at least in principle* be possible to measure its momentum with any desired accuracy before and after the passage of the particle, and thus to predict the momentum of the latter after it has passed through the slit. In fact, such measurements of momentum require only an unambiguous application of the classical law of conservation of momentum, applied for instance to a collision process between the diaphragm and some test body, the momentum of which is suitably controlled before and after the collision. It is true that such a control will essentially depend on an examination of the space-time course of some process to which the ideas of classical mechanics can be applied; if, however, all spatial dimensions and time intervals are taken sufficiently large, this involves clearly no limitation as regards the accurate control of the momentum of the test bodies, but only a renunciation as regards the accuracy of the control of their space-time coordination. This last circumstance is in fact quite analogous to the renunciation of the control of the momentum of the fixed diaphragm in the experimental arrangement discussed above, and depends in the last resort on the claim of a purely classical account of the measuring apparatus, which implies the necessity of allowing a latitude corresponding to the quantum-mechanical uncertainty relations in our description of their behavior.

The principal difference between the two experimental arrangements under consideration is, however, that in the arrangement suited for the control of the momentum of the first diaphragm, this body can no longer be used as a measuring instrument for the same purpose as in the previous case, but must, as regards its position relative to the rest of the apparatus, be treated, like the particle traversing the slit, as an object of investigation, in the sense that the quantum-mechanical uncertainty relations regarding its position and momentum must be taken explicitly into account. In fact, even if we knew the position of the diaphragm relative to the space frame before the first measurement of its momentum, and even though its position after the last measurement can be accurately fixed, we lose, on account of the uncontrollable displacement of the diaphragm during each collision process with the test bodies, the knowledge of its position when the particle passed through the slit. The whole arrangement is therefore obviously unsuited to study the same kind of phenomena as in the previous case. In particular it may be shown that, if the momentum of the diaphragm is measured with an accuracy sufficient for allowing definite conclusions regarding the passage of the particle through some selected slit of the second diaphragm, then even the minimum uncertainty of the position of the first diaphragm compatible with such a knowledge will imply the total wiping out of any interference effect—regarding the zones of permitted impact of the particle on the photographic plate—to which the presence of more than one slit in the second diaphragm would give rise in case the positions of all apparatus are fixed relative to each other.

In an arrangement suited for measurements of the momentum of the first diaphragm, it is further clear that even if we have measured this momentum before the passage of the particle through the slit, we are after this passage still left with a *free choice* whether we wish to know the momentum of the particle or its initial position relative to the rest of the apparatus. In the first eventuality we need only to make a second determination of the momentum of the diaphragm, leaving unknown forever its exact position when the particle passed. In the second eventuality we need only to determine its position relative to the space frame with the inevitable loss of the knowledge of the momentum exchanged between the diaphragm and the particle. If the diaphragm is sufficiently massive in comparison with the particle, we may even arrange the procedure of measurements in such a way that the diaphragm after the first determination of its momentum will remain at rest in some unknown position relative to the

* The obvious impossibility of actually carrying out, with the experimental technique at our disposal, such measuring procedures as are discussed here and in the following does clearly not affect the theoretical argument, since the procedures in question are essentially equivalent with atomic processes, like the Compton effect, where a corresponding application of the conservation theorem of momentum is well established.

other parts of the apparatus, and the subsequent fixation of this position may therefore simply consist in establishing a rigid connection between the diaphragm and the common support.

My main purpose in repeating these simple, and in substance well-known considerations, is to emphasize that in the phenomena concerned we are not dealing with an incomplete description characterized by the arbitrary picking out of different elements of physical reality at the cost of sacrifying other such elements, but with a rational discrimination between essentially different experimental arrangements and procedures which are suited either for an unambiguous use of the idea of space location, or for a legitimate application of the conservation theorem of momentum. Any remaining appearance of arbitrariness concerns merely our freedom of handling the measuring instruments, characteristic of the very idea of experiment. In fact, the renunciation in each experimental arrangement of the one or the other of two aspects of the description of physical phenomena,—the combination of which characterizes the method of classical physics, and which therefore in this sense may be considered as *complementary* to one another,—depends essentially on the impossibility, in the field of quantum theory, of accurately controlling the reaction of the object on the measuring instruments, i.e., the transfer of momentum in case of position measurements, and the displacement in case of momentum measurements. Just in this last respect any comparison between quantum mechanics and ordinary statistical mechanics,—however useful it may be for the formal presentation of the theory,—is essentially irrelevant. Indeed we have in each experimental arrangement suited for the study of proper quantum phenomena not merely to do with an ignorance of the value of certain physical quantities, but with the impossibility of defining these quantities in an unambiguous way.

The last remarks apply equally well to the special problem treated by Einstein, Podolsky and Rosen, which has been referred to above, and which does not actually involve any greater intricacies than the simple examples discussed above. The particular quantum-mechanical state of two free particles, for which they give an explicit mathematical expression, may be reproduced, at least in principle, by a simple experimental arrangement, comprising a rigid diaphragm with two parallel slits, which are very narrow compared with their separation, and through each of which one particle with given initial momentum passes independently of the other. If the momentum of this diaphragm is measured accurately before as well as after the passing of the particles, we shall in fact know the sum of the components perpendicular to the slits of the momenta of the two escaping particles, as well as the difference of their initial positional coordinates in the same direction; while of course the conjugate quantities, i.e., the difference of the components of their momenta, and the sum of their positional coordinates, are entirely unknown.* In this arrangement, it is therefore clear that a subsequent single measurement either of the position or of the momentum of one of the particles will automatically determine the position or momentum, respectively, of the other particle with any desired accuracy; at least if the wave-length corresponding to the free motion of each particle is sufficiently short compared with the width of the slits. As pointed out by the named authors, we are therefore faced at this stage with a completely free choice whether we want to determine the one or the other of the latter quantities by a process which does not directly interfere with the particle concerned.

Like the above simple case of the choice between the experimental procedures suited for the prediction of the position or the momentum of a single particle which has passed through a slit in a diaphragm, we are, in the "freedom of choice" offered by the last arrangement, just concerned with a *discrimination between different experimental procedures which allow of the unambiguous use of complementary classical concepts.* In fact to measure the position of one of the particles can mean nothing else than to establish a correlation between its behavior and some

* As will be seen, this description, apart from a trivial normalizing factor, corresponds exactly to the transformation of variables described in the preceding footnote if $(q_1 p_1)$, $(q_2 p_2)$ represent the positional coordinates and components of momenta of the two particles and if $\theta = -\pi/4$. It may also be remarked that the wave function given by formula (9) of the article cited corresponds to the special choice of $P_2 = 0$ and the limiting case of two infinitely narrow slits.

instrument rigidly fixed to the support which defines the space frame of reference. Under the experimental conditions described such a measurement will therefore also provide us with the knowledge of the location, otherwise completely unknown, of the diaphragm with respect to this space frame when the particles passed through the slits. Indeed, only in this way we obtain a basis for conclusions about the initial position of the other particle relative to the rest of the apparatus. By allowing an essentially uncontrollable momentum to pass from the first particle into the mentioned support, however, we have by this procedure cut ourselves off from any future possibility of applying the law of conservation of momentum to the system consisting of the diaphragm and the two particles and therefore have lost our only basis for an unambiguous application of the idea of momentum in predictions regarding the behavior of the second particle. Conversely, if we choose to measure the momentum of one of the particles, we lose through the uncontrollable displacement inevitable in such a measurement any possibility of deducing from the behavior of this particle the position of the diaphragm relative to the rest of the apparatus, and have thus no basis whatever for predictions regarding the location of the other particle.

From our point of view we now see that the wording of the above-mentioned criterion of physical reality proposed by Einstein, Podolsky and Rosen contains an ambiguity as regards the meaning of the expression "without in any way disturbing a system." Of course there is in a case like that just considered no question of a mechanical disturbance of the system under investigation during the last critical stage of the measuring procedure. But even at this stage there is essentially the question of *an influence on the very conditions which define the possible types of predictions regarding the future behavior of the system.* Since these conditions constitute an inherent element of the description of any phenomenon to which the term "physical reality" can be properly attached, we see that the argumentation of the mentioned authors does not justify their conclusion that quantum-mechanical description is essentially incomplete. On the contrary this description, as appears from the preceding discussion, may be characterized as a rational utilization of all possibilities of unambiguous interpretation of measurements, compatible with the finite and uncontrollable interaction between the objects and the measuring instruments in the field of quantum theory. In fact, it is only the mutual exclusion of any two experimental procedures, permitting the unambiguous definition of complementary physical quantities, which provides room for new physical laws, the coexistence of which might at first sight appear irreconcilable with the basic principles of science. It is just this entirely new situation as regards the description of physical phenomena, that the notion of *complementarity* aims at characterizing.

The experimental arrangements hitherto discussed present a special simplicity on account of the secondary role which the idea of time plays in the description of the phenomena in question. It is true that we have freely made use of such words as "before" and "after" implying time-relationships; but in each case allowance must be made for a certain inaccuracy, which is of no importance, however, so long as the time intervals concerned are sufficiently large compared with the proper periods entering in the closer analysis of the phenomenon under investigation. As soon as we attempt a more accurate time description of quantum phenomena, we meet with well-known new paradoxes, for the elucidation of which further features of the interaction between the objects and the measuring instruments must be taken into account. In fact, in such phenomena we have no longer to do with experimental arrangements consisting of apparatus essentially at rest relative to one another, but with arrangements containing moving parts,—like shutters before the slits of the diaphragms,—controlled by mechanisms serving as clocks. Besides the transfer of momentum, discussed above, between the object and the bodies defining the space frame, we shall therefore, in such arrangements, have to consider an eventual exchange of energy between the object and these clock-like mechanisms.

The decisive point as regards time measurements in quantum theory is now completely analogous to the argument concerning measurements of positions outlined above. Just as the transfer of momentum to the separate parts of

the apparatus,—the knowledge of the relative positions of which is required for the description of the phenomenon,—has been seen to be entirely uncontrollable, so the exchange of energy between the object and the various bodies, whose relative motion must be known for the intended use of the apparatus, will defy any closer analysis. Indeed, it is *excluded in principle to control the energy which goes into the clocks without interfering essentially with their use as time indicators*. This use in fact entirely relies on the assumed possibility of accounting for the functioning of each clock as well as for its eventual comparison with other clocks on the basis of the methods of classical physics. In this account we must therefore obviously allow for a latitude in the energy balance, corresponding to the quantum-mechanical uncertainty relation for the conjugate time and energy variables. Just as in the question discussed above of the mutually exclusive character of any unambiguous use in quantum theory of the concepts of position and momentum, it is in the last resort this circumstance which entails the complementary relationship between any detailed time account of atomic phenomena on the one hand and the unclassical features of intrinsic stability of atoms, disclosed by the study of energy transfers in atomic reactions on the other hand.

This necessity of discriminating in each experimental arrangement between those parts of the physical system considered which are to be treated as measuring instruments and those which constitute the objects under investigation may indeed be said to form a *principal distinction between classical and quantum-mechanical description of physical phenomena*. It is true that the place within each measuring procedure where this discrimination is made is in both cases largely a matter of convenience. While, however, in classical physics the distinction between object and measuring agencies does not entail any difference in the character of the description of the phenomena concerned, its fundamental importance in quantum theory, as we have seen, has its root in the indispensable use of classical concepts in the interpretation of all proper measurements, even though the classical theories do not suffice in accounting for the new types of regularities with which we are concerned in atomic physics. In accordance with this situation there can be no question of any unambiguous interpretation of the symbols of quantum mechanics other than that embodied in the well-known rules which allow to predict the results to be obtained by a given experimental arrangement described in a totally classical way, and which have found their general expression through the transformation theorems, already referred to. By securing its proper correspondence with the classical theory, these theorems exclude in particular any imaginable inconsistency in the quantum-mechanical description, connected with a change of the place where the discrimination is made between object and measuring agencies. In fact it is an obvious consequence of the above argumentation that in each experimental arrangement and measuring procedure we have only a free choice of this place within a region where the quantum-mechanical description of the process concerned is effectively equivalent with the classical description.

Before concluding I should still like to emphasize the bearing of the great lesson derived from general relativity theory upon the question of physical reality in the field of quantum theory. In fact, notwithstanding all characteristic differences, the situations we are concerned with in these generalizations of classical theory present striking analogies which have often been noted. Especially, the singular position of measuring instruments in the account of quantum phenomena, just discussed, appears closely analogous to the well-known necessity in relativity theory of upholding an ordinary description of all measuring processes, including a sharp distinction between space and time coordinates, although the very essence of this theory is the establishment of new physical laws, in the comprehension of which we must renounce the customary separation of space and time ideas.*

* Just this circumstance, together with the relativistic invariance of the uncertainty relations of quantum mechanics, ensures the compatibility between the argumentation outlined in the present article and all exigencies of relativity theory. This question will be treated in greater detail in a paper under preparation, where the writer will in particular discuss a very interesting paradox suggested by Einstein concerning the application of gravitation theory to energy measurements, and the solution of which offers an especially instructive illustration of the generality of the argument of complementarity. On the same occasion a more thorough discussion of space-time measurements in quantum theory will be given with all necessary mathematical developments and diagrams of experimental

The dependence on the reference system, in relativity theory, of all readings of scales and clocks may even be compared with the essentially uncontrollable exchange of momentum or energy between the objects of measurements and all instruments defining the space-time system of reference, which in quantum theory confronts us with the situation characterized by the notion of complementarity. In fact this new feature of natural philosophy means a radical revision of our attitude as regards physical reality, which may be paralleled with the fundamental modification of all ideas regarding the absolute character of physical phenomena, brought about by the general theory of relativity.

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arrangements, which had to be left out of this article, where the main stress is laid on the dialectic aspect of the question at issue.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Selective X-Ray Diffraction from Artificially Stratified Metal Films Deposited by Evaporation

In a search for a new method of determining absolute x-ray wave-lengths we have produced stratified metal films on glass consisting of one hundred layers of gold alternating with one hundred layers of copper by evaporation and have obtained selective x-ray diffraction of molybdenum K radiation in the first order from them.

We chose gold and copper because these metals are isomorphs almost indistinguishable from each other as to their external fields which determine mutual cohesive and adhesive forces. We hoped thus to avoid coherence of the layers into islands. We intend soon, however, to try pairing nonisomorphic atoms to form stratified films.

The copper, evaporated in vacuum from a molybdenum trough of "V" cross section heated by electrical conduction was deposited without interruption on the under surface of a 5-cm square of plate glass distant about 12.5 cm. Simultaneously the gold was deposited in intermittent spurts on the same glass plate from a similar molybdenum trough near the first one by periodically raising and lowering the heating current on the second trough just enough alternately to produce and inhibit boiling of the gold. This intermittent heating was timed by a pendulum clock mechanism. Thermojunctions placed near the troughs permitted us to check and control the uniformity of the temperature regime of the copper and gold boilers during the deposition.

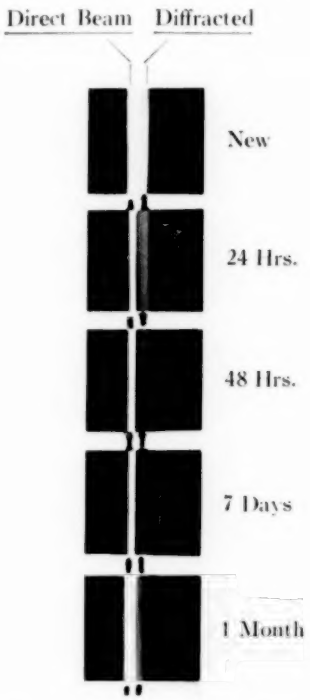

FIG. 1. X-ray spectra of molybdenum K radiation made with artificially stratified metal films deposited by evaporation.

At the end of every twenty-five layers of gold a light aluminum vane shielding one corner of the glass plate was shifted a little by means of magnets so as to form a "staircase" with steps 25 layers high in the deposit in this region, to check the uniformity of deposition by interferometry with visible light and also to determine to what extent the change of phase of the light at reflection on each step might be influenced by the varying proximity of the glass backing. Rough estimates of thickness of the entire deposit made by placing an optical flat against the film and observing the fringe shift across the steps of the staircase give a total thickness of roughly 10,000A, and hence a "grating constant" of 100A. The total stratified deposits transmit light appreciably.

The films were examined for selective x-ray reflection with K radiation from a molybdenum target tube and an improvised Bragg type rocking crystal spectrograph having an especially designed shielding mechanism preventing fogging of the diffracted spectrum at such small angles by direct radiation. Control exposures showing no diffraction maxima like those obtained with the stratified films were made with (1) clean glass, (2) a pure evaporated copper deposit on glass, (3) a copper plate, (4) nothing whatever, (5) a calcite crystal (cleavage surface), etc. *The reality of the diffraction maxima is clinched by the interesting fact shown in Fig. 1, that the intensity of these diffracted images falls off approximately exponentially with time, with "half-life" of roughly two or three days.* Ten minutes suffices to give a good photographic exposure hence this instability is no bar to their use. The *sharpness* of the diffracted image does not change materially; only the intensity diminishes, as if the amplitude of the strata were obliterated by diffusion. *It would seem likely that we have here an excellent way of studying intimately the diffusion of atoms in the solid state.*

The photographs indicate a grating constant in accord with the 100A computed above from the total thickness of the deposit. The fuzziness of the layers probably explains the absence of higher orders.

We are indebted to Dr. Leon L. Watters of New York City for the funds which have supported this work.

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J. PAUL YOUTZ
California Institute of Technology,
September 2, 1935.

Velocity of Slow Neutrons by Mechanical Velocity Selector

Four duraluminum disks were provided with sectors of sheet cadmium, the sectors subtending 3.7° with spacing of 3.5° between. Two of these disks were mounted 54 cm apart to rotate on the same shaft, while the other two disks were fixed within 5 mm of the rotating disks, respectively, as shown in Fig. 1. Since the cadmium is practically opaque to slow neutrons and the duraluminum transparent, the two pairs of disks form a mechanical velocity selector for slow neutrons. Speeds up to 5000 r.p.m. were used.

The Rn-Be source, about 600 millicuries, was placed in a Cd shielded paraffin cylinder 16 cm diameter and 22 cm long, and the neutrons were detected by an 8-cm diameter Li-lined ion chamber specially constructed to be insensitive to noise and connected to a linear amplifier-thyratron recording system.

Better resolution is desirable, but decreasing the ratio of width of spacing to width of Cd sectors not only reduces the number of slow neutrons as the cube of this ratio, but unfortunately leaves unchanged the large background count due to neutrons of intermediate and high velocities which are not appreciably absorbed by the Cd sectors. These background counts due to the disintegration of Li and the projection of various nuclei[1] by these higher speed neutrons were in these experiments slightly larger than the counts due to slow neutrons. For example, about 29.25 counts per minute were recorded with the selector operating slowly, around 250 r.p.m., about 24.7 counts per minute were obtained at 2500 r.p.m., and a background of about 16 counts per minute was obtained with a piece of Cd interposed.

The results prove by direct measurement that many of the slow neutrons are in the thermal velocity range. The curve in Fig. 2 shows the decrease in the number of slow neutrons detected at various speeds of the selector disks. When the selector is run at a speed of about 2500 to 3000 r.p.m., such that it intercepts best particles with speeds of 225,000 to 270,000 cm/sec., there is the greatest decrease in the number of slow neutrons coming through. Hence the peak of the velocity distribution of these slow neutrons is in this region, which corresponds to the maximum of the velocity distribution to be expected if the neutrons were in thermal equilibrium in the paraffin. The precision in these experiments is not very high, and the exact energy distribution curve will require further data and further analysis.

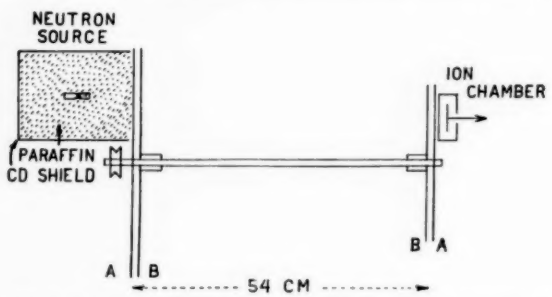

FIG. 1. Schematic drawing of mechanical velocity selector for slow neutrons. *A*, rotating disk with Cd sectors; *B*, fixed disk with Cd sectors.

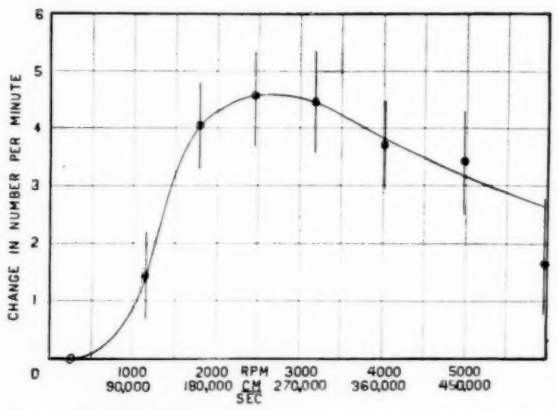

FIG. 2. Curve showing change (decrease) in number of slow neutrons detected after passing through the two shutter systems, as the speed of the sectors was changed. The speed of the sectors is indicated in revolutions per minute, and the neutron velocity for which the selector is most effective is also indicated.

The vertical lines indicate the probable precision calculated on the basis of the square root of the number of counts.

The curve appears to indicate that on the high velocity side the number of neutrons falls off much less rapidly than in a Maxwell (v^3) distribution.[2] This is probably to be expected since there are still many fast neutrons traversing the paraffin and therefore many at intermediate velocities and not yet in thermal equilibrium. The low velocity end of the curve may well indicate a sharper decrease than the Maxwellian curve. The combination of the slower neutrons with H or C nuclei would give this.

Obviously the sensitivity function of the Li detector for varying neutron velocities may influence a curve such as that of Fig. 2, but such evidence as there is does not indicate much change of Li sensitivity in the Cd absorption range.

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October 7, 1935.

[1] Dunning, Pegram, Fink and Mitchell, Phys. Rev. **48**, 265 (1935).
[2] Fraser, *Molecular Rays*, pp. 64.

β-Radioactivity of Neutrons

In a recent paper Konopinski and Uhlenbeck[1] have proposed a modification of the Fermi interaction "Ansatz" which leads to improved agreement with experiments on electron and positron emission from nuclei. The new expression for the interaction operator is[2]

$$H=Q[B_0+(\boldsymbol{\alpha}_{\text{heavy}}\cdot\mathbf{B})]+Q^*[B_0^*+(\boldsymbol{\alpha}_{\text{heavy}}\cdot\mathbf{B})^*]$$

where $B_0=(\partial\phi^*/\partial t)\beta\psi$, $\mathbf{B}=\text{grad}\,\phi^*\beta\psi$. (1)

In this note we shall discuss the following processes. (a) $N\rightarrow P+\epsilon^-+n'$; (b) $P\rightarrow N+\epsilon^++n$; and (c) $P+n'\rightarrow N+\epsilon^+$

where n and n' denote neutrino and antineutrino, respectively. The processes (a) and (b) were considered by Wolfe and Uhlenbeck[3] on the basis of the original Fermi theory.

For processes (a) and (b) we find for the reciprocal of the lifetime

$$(mc^2/tr)G^2[\tfrac{1}{2}(\eta_0^2+1)^{3/2}\operatorname{arcsinh}\eta_0+\tfrac{1}{4}(\eta_0^2+1)^{1/2}\operatorname{arcsinh}\eta_0 +(1/105)\eta_0^7-(1/15)\eta_0^5-\tfrac{3}{4}\eta_0^3-\tfrac{3}{4}\eta_0]. \quad (2)$$

G is the dimensionless constant $gm^2c/(2\pi^3)^{1/2}\hbar^3=10^{-13}$ and η_0 is $(\Delta^2-1)^{1/2}$ where $m\Delta$ is the mass difference of proton and neutron. Transitions (a) and (b) can occur only if $\Delta>1$, either one occurring depending on the sign of the mass difference. One can obtain this formula by putting $|M|^2=1$ and integrating Eq. (12) of Konopinski's and Uhlenbeck's paper from 1 to W_0.

For small values of $(\Delta-1)$ the lifetime is given by

$$\tau=10^6(\Delta-1)^{-11/2}. \quad (3)$$

Taking for the masses of the neutron and proton the recent values given by Bethe[4] we find for the lifetime from Eq. (2)

$$\tau=3\times10^5 \text{ seconds}. \quad (4)$$

or about $3\frac{1}{2}$ days. This value, unfortunately, is much too large to be verified experimentally at present.

The process (c) will occur when the antineutrinos accompanying beta-rays collide with a nucleus. The result of this collision will be the absorption of the antineutrino with the emission of a positron. The cross section for this process is

$$\sigma\sim G^2(\hbar/mc)^2. \quad (5)$$

which is of the order of 10^{-47} cm^2. This is smaller than the cross section for the creation of pairs by beta-rays by a factor of about 10^{-18}.[5]

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August 27, 1935.

[1] Konopinski and Uhlenbeck, Phys. Rev. **48**, 7 (1935).
[2] In reference 1 the formulae defining B_0, **B** and B_0^*, **B*** have to be interchanged.
[3] Wolfe and Uhlenbeck, Phys. Rev. **46**, 237 (1934).
[4] Bethe, Phys. Rev. **47**, 633 (1935).
[5] Nordheim, J. de physique **6**, 135 (1935).

A New Radio Transmission Phenomenon

A remarkable vagary of radio transmission has recently been found to occur at regular intervals, separated in time by twice the sun's rotation period. It is a world-wide phenomenon, or more accurately semi-world-wide, as it involves all high frequency radio transmission over the illuminated half of the globe and not the dark half. Depending apparently on some solar emanation lasting only a few minutes, it may be of interest to workers in sciences other than radio. In fact, its thorough elucidation appears to call for the study of such cosmic data as solar radiation intensities, terrestrial magnetism, atmospheric ionization, aurora, earth currents, etc.

If the next manifestation occurs in accordance with the cycle appearing in the last four occurrences, it will be some time between October 21 and 25. It is therefore suggested to those concerned with observations in the above fields as well as in long-distance radio propagation that they make special efforts to make continuous observations on these dates.

The phenomenon is a sudden disappearance of radio signals for several minutes, the complete process of fading out and reappearing occupying about 15 minutes. It occurred on March 20, May 12, July 6, and August 30. The time intervals between these dates are close to 54 days, twice the period of rotation of the sun.

The phenomenon was first brought to my attention by a correspondent in France, who reported that on May 12 in the receiving station near Paris all high frequency reception suddenly disappeared, so rapidly "that the surprised operator thought at first that a fuse had blown" in the receiving station. Beginning at 1157 GMT received signals disappeared completely in three minutes and then after a few minutes reappeared slowly, resuming normal intensity at 1215 GMT. I subsequently learned, through the courtesy of Mr. H. H. Beverage, Chief Research Engineer, that the same thing occurred in the R. C. A. Communications Inc. receiving station at Riverhead, N. Y., and from Mr. L. Espenschied, Radio Transmission Development Director of the Bell Telephone Laboratories that it also occurred in their receiving station at Netcong, N. J., at precisely the same time.

It was subsequently learned that these fadeouts had occurred also on March 20 at 0150 to 0205 GMT, and on July 6 at 1409 to 1425 GMT. The 54-day period was noticed and radio operators were requested to be on the watch for a similar occurrence during August 28 to 30. It duly put in its appearance on August 30, as reported by Mr. Beverage, lasting from 2320 to 2335 GMT.

The sudden intense disturbance causing these 15-minute anomalies in radio reception must have other effects, but none have so far been found. They occur in general during periods, lasting several hours or days, of terrestrial magnetic disturbance and of fluctuating earth currents, but no sharp anomalies in these quantities during the 15-minute period of the radio fadeout have been traced.

Perhaps the chief mystery in this phenomenon is why only one has occurred in every two solar rotation periods, throughout a total of seven periods. It may be merely fortuitous, and it would be desirable to look for it at 27-day intervals, say October 21–25, November 17–21, and December 14–18. Special interest will attach to determining whether it occurs at the next indicated time, October 21 to 25. It would be very desirable that observations, as nearly continuous as practicable, be made of high frequency radio intensities, solar radiation intensities, terrestrial magnetism, atmospheric ionization, earth currents, etc. I would be very glad to have anyone interested communicate with me on the subject.

J. H. DELLINGER

U. S. Department of Commerce,
September 21, 1935.

Two New Bands of CO_2 in the Photographic Infrared

Recently in this journal Adel and Slipher[1] have announced the observation of one of the Venus CO_2 bands in absorption in the laboratory with a path-length of 45 m and a pressure of 42 atmos. It is the rotation-vibration-band $5\nu_3$ according to Dennison's nomenclature. With the aid of the new Agfa infrared plates we have photographed *two new CO_2 bands* at 1.2031μ and 1.2178μ using only a path-length of 4 m and a pressure of 1 to 10 atmos. At 1 atmos. pressure the fine structure of the bands is clearly to be seen on our plates, but too faint to measure. With increasing pressure the lines broaden very much so that at 10 atmos. pressure, when the intensity of absorption is fairly strong, the fine structure is not any more resolved and so cannot be measured. At this high pressure there appears, however, a comparatively sharp edge at the high frequency side of the band. This evidently corresponds to the head of the band, the convergence in the line series, being caused by the difference in the moments of inertia in the upper and lower states. The wave-lengths given above refer to these band heads.

Adel and Dennison[2] have calculated a formula representing all the observed infrared CO_2 bands known at that time. They have *predicted* the position of certain other bands, among others the pair of bands $3\nu_3+(\nu_1;\ 2\nu_2)$ at 8291 cm^{-1} and 8188 cm^{-1}. The wave-lengths of the observed heads correspond to 8309 and 8209 cm^{-1}. There can therefore be no question that the new bands are $3\nu_3+(\nu_1;\ 2\nu_2)$, the difference of the observed and calculated frequencies mainly arising from the fact, that not zero lines but band heads were measured. The distance of the head from the zero line can approximately be calculated from rough B values which can be interpolated from the data given by Adel and Dennison.[3] We obtain $\nu_{head}-\nu_0{}^+=16$ cm^{-1}, so that the frequencies of the zero lines of the observed bands become 8293 and 8193 cm^{-1}. This agrees satisfactorily with the values predicted by Adel and Dennison.

It is interesting to stress that the bands $5\nu_3+(\nu_1;\ 2\nu_2)$ occurring in the spectrum of the planet Venus but *not* observed by Adel and Slipher in the laboratory are at least 400 times less intense than the pair $3\nu_3+(\nu_1;\ 2\nu_2)$ found by us.

G. HERZBERG
H. VERLEGER
Physikalisches Institut der Techn. Hochschule,
Darmstadt, Germany,
July 27, 1935.

[1] A. Adel and V. M. Slipher, Phys. Rev. **46**, 240 (1934).
[2] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933).
[3] A. Adel and D. M. Dennison, Phys. Rev. **44**, 99 (1933).

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